

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A I—General, Physical, and Inorganic Chemistry

JANUARY, 1944.

I.—SUB-ATOMICS.

Comparison of the prototype metre with the wave-length of the red line of cadmium. M. F. Romanova, G. V. Varlich, A. I. Kartashev, and N. R. Batartschukova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **37**, 46—51).—A high-precision method based on interference and reflexion photographs is described. Data for measurements in air and in vac. taken at intervals over 2 years give: in air $\lambda = 6438.4687$, in vac. $\lambda = 6440.2488$ Å., in accord with the results of previous investigators. λ can be expressed in terms of a metre fraction with an accuracy of ± 0.0004 Å. N. M. B.

Transition probabilities in the subordinate series of thallium. G. S. Kvater (*J. Physics U.S.S.R.*, 1942, **6**, 145—162).—Measurements of the anomalous dispersion of the lines $\lambda 3776$ and $\lambda 5350$ Å. of Tl are used for the determination of the abs. transition probabilities, 0.0417 and 0.0424, respectively. Equations for the temp. variation of the optical densities for these frequencies lead to the evaluation of the heat of evaporation at abs. zero (43,390 g.-cal.). An equation for the v.p. of Tl at $612-1063^\circ$ C. is derived. Boltzmann's law is confirmed for the distribution of atoms in the levels $6^2P_{1/2}$ and $6^2P_{3/2}$, and a val. for the ratio h/k (4.82×10^{-11} degree-sec.) is deduced. The sum rule does not hold for the sharp or diffuse subordinate series of Tl I. H. J. W.

Spectra of the rare gases and their Zeeman effects. J. B. Green (*Physical Rev.*, 1943, [ii], **64**, 151—155).—The Zeeman effect of the rare gases is discussed on the basis of the Shortley-Fried coupling scheme (cf. A., 1939, I, 1). Matrices for this type of interaction and the g factors from the transformation to LS coupling for the p^6f configurations are calc. The derived Paschen-Back patterns agree well with observed structures. N. M. B.

Mercury arc cathode. C. G. Smith (*Physical Rev.*, 1943, [ii], **64**, 40; cf. A., 1942, I, 381).—A correction. N. M. B.

Electric breakdown and cumulative ionisation. B. Davydov (*Physical Rev.*, 1943, [ii], **64**, 156—158).—Mathematical. Calculations lead to an interpretation of the breakdown as a transition from the lower to the upper branch of an S-like current-field strength curve. An expression for the breakdown field strength is obtained. N. M. B.

Shape of betatron pole faces. J. H. Bartlett (*Physical Rev.*, 1943, [ii], **64**, 185; cf. Kerst, A., 1941, I, 358).—The requirements to be fulfilled by the magnetic field near the electron beam as related to the shape of pole face are calc. N. M. B.

Report of the Committee on at. wts. of the American Chemical Society. G. P. Baxter (*J. Amer. Chem. Soc.*, 1943, **65**, 1443—1447).—The period since September, 1940, is reviewed for C, O, F, Zn, Ag, Br, K, Sm, Ga, Yb, and Pb. The val. of 65.377 for Zn is 0.05 > the mass-spectral val. of 65.33. The val. for Sm is probably 0.05 < the present val. of 150.43, and that for Yb 0.06 higher. W. R. A.

Spontaneous fission of uranium and thorium. G. N. Flerov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **37**, 58; cf. A., 1941, I, 287; 1942, I, 5).—The possibility of a difference between the spectra of fragments obtained by spontaneous fission and by induced fission is postulated and an explanation proposed. N. M. B.

Neutron polarisation and ferromagnetic saturation. F. Bloch, M. Hamermesh, and H. Staub (*Physical Rev.*, 1943, [ii], **64**, 47—56).—The transmission of thermal neutrons through magnetised Fe was measured in its dependence on % deviation from saturation and on the thickness of the sample. Results agree with the theory of Halpern and Holstein (cf. A., 1941, I, 359). Terms in the theoretical expression are evaluated. The calc. linear dimensions of the micro-crystals is 1.4×10^{-4} cm. N. M. B.

Branching ratio of ^{22}Na . H. Weltin (*Physical Rev.*, 1943, [ii], **64**, 128).—Using micro-gas analysis, the amount of Ne was compared with the no. of positrons emitted for the decay reactions $^{22}\text{Na} \rightarrow ^{22}\text{Ne} + e^+$, $^{22}\text{Na} + e^- \rightarrow ^{22}\text{Ne}$. Results show that the ratio of the no. of nuclei excited to the no. of positrons emitted is 3.2. This supports the Fermi β -decay theory, provided that the change in nuclear spin is $\Delta i = 1$. N. M. B.

Energies of the γ -rays from radioactive scandium, gallium, tungsten, and lanthanum. C. E. Mandeville (*Physical Rev.*, 1943, [ii], **64**, 1

147—151).—Energies determined by the method of semicircular focussing of Compton recoils in a magnetic spectrograph are: ^{48}Sc , 1.35 ± 0.03 ; ^{72}Ga , 1.17 ± 0.02 and 2.65 ± 0.06 ; ^{187}W , 0.94 ± 0.02 ; ^{140}La , 2.04 ± 0.04 Me.v. The quanta emitted by ^{72}Ga are present with equal intensity, suggesting that they may be in cascade. The γ -ray activity of ^{72}Ga has a half-period of 14.25 ± 0.20 hr. N. M. B.

Nuclear chemistry. R. Fleischmann (*Angew. Chem.*, 1940, **53**, 485—498).—A lecture.

Altitude-dependence of Auger showers and the primary spectrum of cosmic radiation. D. V. Skobeltzin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **37**, 52—57; cf. A., 1943, I, 294).—Mathematical. N. M. B.

Large cosmic-ray bursts in an unshielded ionisation chamber. R. E. Lapp (*Physical Rev.*, 1943, [ii], **64**, 129—130).—The bursts coincide with extensive atm. (Auger) showers as detected with Geiger-Müller counters, and represent regions of very high particle density in an Auger shower. N. M. B.

Theory of cosmic-ray mesons. J. Hamilton, W. Heitler, and H. W. Peng (*Physical Rev.*, 1943, [ii], **64**, 78—94).—Mathematical. The quantum theory of damping is applied to the production of mesons by proton-proton collisions. The variation of meson intensity with energy, height, and geomagnetic latitude is in good agreement with experiment. Decay of transverse mesons, which have a very short lifetime, accounts satisfactorily for the soft component in the high atm. Meson showers, transformation into neutrons, and other effects are discussed. N. M. B.

Production of mesons by proton-proton collisions. W. Heitler and H. W. Peng (*Proc. Roy. Irish Acad.*, 1943, **49**, A, 101—133).—Mathematical. The meson spectrum of a moving nucleon is obtained by a method similar to that used by Weizsäcker (A., 1934, 712) for collisions of fast electrons. A fast-moving nucleon can be considered as being equiv. to a free meson pulse moving in the same direction. The scattering of a meson by a nucleon, the production of mesons by collision of two nucleons, and the energy loss of the nucleon are considered. A. J. M.

Dipole character of the mesotron and the polarisation of vacuum. D. Ivanenko and A. Sokolov (*J. Physics, U.S.S.R.*, 1942, **6**, 175—179).—Theoretical. An effective dipole moment for the mesotron is deduced from Proca equations, and its effect on nuclear and electromagnetic processes is discussed. Smaller cross-sections at high energies follow from damping effects and by introducing the higher excited nucleon states postulated by Heitler. L. J. J.

Pseudo-scalar theory of the mesotron. V. L. Ginzburg (*J. Physics, U.S.S.R.*, 1942, **6**, 180—184).—Interactions of mesotrons with photons and with heavy particles are discussed on the basis of a pseudo-scalar wave-function for the mesotron. Its application to mesotron spin and excited states of heavy particles is discussed. L. J. J.

Observable magnitudes in the theory of elementary particles. II. W. Heisenberg (*Z. Physik*, 1943, **120**, 673—702; cf. A., 1943, I, 271).—The author's η -matrix wave theory is applied to scattering of elementary particles on the basis of two types of interaction. A δ -function interaction leads to results corresponding with those given by existing theory. The second type of interaction gives effective cross-sections tending to limiting vals. at high energies. Formation of new particles may have an explosive multiple character at high collision energies. The theory is free from divergence difficulties. L. J. J.

II.—MOLECULAR STRUCTURE.

Spectral and collision data of CO^+ and dissociation energy of carbon monoxide. R. K. Asundi (*Proc. Indian Acad. Sci.*, 1943, **18**, A, 8—10).—Vals. for the dissociation energy of CO deduced from extrapolation of spectral data of $^2\Sigma^+$ and $^2\Pi$ states of CO^+ are 10.45 and 10.4 e.v., and from collision data involving the same states, 9.75 and 9.7 e.v., respectively. L. J. J.

Excitation processes in the night sky and the aurora. T. Y. Wu (*Proc. Indian Acad. Sci.*, 1943, **18**, A, 40—66).—The forbidden O I lines, the N_2 , N_2^+ , and O_2 band systems, and the anomalous

intensity features, characteristic of night-sky and auroral spectra, can be explained on the basis of collisions of the second kind between metastable O and N atoms and mols. The latter are formed by recombination of atoms formed by photo-dissociation during the day, and produce the former in collision among themselves. L. J. J.

Nuclear spin of ^{37}Cl . E. F. Shrader (*Physical Rev.*, 1943, [ii], **64**, 57—59).—The nuclear spin was determined by observing the line intensities in the band spectrum of $^{36}\text{Cl}_2$ and in that of Cl_2 gas containing 45% of $^{37}\text{Cl}_2$. The alternating intensity ratio vals. for lines of odd and even J vals. were 1:26 for $^{36}\text{Cl}_2$ and 1:28 for $^{37}\text{Cl}_2$, indicating that the nuclear spin is 5/2 in each case. N. M. B.

Light absorption of nickel thiocyanate solutions. II. Non-aqueous solutions. A. von Kiss and P. Csokan (*Z. anorg. Chem.*, 1941, **247**, 205—210; cf. A., 1942, I, 205).—The extinction curves of $\text{Ni}(\text{CNS})_2$ in H_2O and in various H_2O -non-electrolyte mixtures, and of anhyd. $\text{Ni}(\text{CNS})_2$ in org. solvents, were determined. The org. substances used were MeOH , EtOH , PrOH , $\text{CO}(\text{NH}_2)_2$, COMe , $\text{C}_6\text{H}_5\text{N}$, quinoline, and glycerol. The alteration of the extinction curves in the org. solvents is due to the formation of the complex $[\text{Ni}(\text{CNS})_2\text{L}_2]$ where L is the org. solvent. In presence of excess of CNS' ions the complex $[\text{Ni}(\text{CNS})_4]^{2-}$ generally arises. In some solvents the complex $[\text{Ni}(\text{CNS})_4\text{L}_2]^{2-}$ occurs. J. F. H.

Effect of oxygen on the fluorescence of hydrocarbons. J. A. Miller and C. A. Baumann (*J. Amer. Chem. Soc.*, 1943, **65**, 1540—1546).—Intensity of fluorescence of 3:4-benzpyrene, 20-methylcholanthrene, 9:10-dimethyl-1:2-benzanthracene, 1:2:5:6-dibenzanthracene, 1:2-benzanthracene, and anthracene in several solvents, and in the presence and absence of air, has been measured. In air intensities are $\frac{1}{2}$ — $\frac{1}{3}$ those in the absence of air, but quenching does not always follow solubility of O_2 . SO_2 is a more effective inhibitor than O_2 , whilst HCl and NMe_3 are less effective. Inhibition changes reversibly with partial pressure of the gas. Equations relating intensity of fluorescence and partial pressure of O_2 are derived, and agree well with experimental data. The fluorescence in ligroin and $\text{C}_6\text{H}_5\text{N}$ of the non-saponifiable residue from mouse tissue is investigated, and does not show sensible variation with the pressure of O_2 . W. R. A.

Fluorescence of monomethincyanines, especially reversible polymerides. I. F. Katheder (*Kolloid-Z.*, 1940, **92**, 299—324). Solutions of NN' -methylene- ψ -isocyanine chloride (I) (quinoline-red) exhibit normal liquid fluorescence, excitable by any λ corresponding with the absorption. The intensity decreases with increasing concn., and is markedly affected by the solvent and by foreign substances. The influence of temp. is negligibly small. NN' -Diethyl- ψ -isocyanine chloride (II) and -mononaphtho- ψ -isocyanine chloride (III) both show resonance fluorescence, the intensity of which increases with concn. to a max. and then falls. Dil. solutions of (II) and (III) are very temp.-sensitive, and may show a decrease of 10—15% in intensity for 1° rise; more conc. solutions are less sensitive. The fluorescence is due to polymerised mols., which do not occur in (I), and the effect of temp. is due to depolymerisation, which is hindered in more conc. solutions by their high viscosity. The quenching of the fluorescence of (I) by H^+ , OH^+ , and $\alpha\text{-C}_6\text{H}_4(\text{OH})_2$ has been studied and is discussed theoretically. F. L. U.

Mechanism of luminescence of phosphors. V. V. Antonov-Romanovski (*J. Physics, U.S.S.R.*, 1942, **6**, 120—140).—A detailed account of work already noted (A., 1943, I, 114). H. J. W.

Luminescence of fluorspars. V. P. Rvatshev (*J. Physics, U.S.S.R.*, 1942, **6**, 141—144).—Two types of ultra-violet luminescence of natural CaF_2 are found; all specimens examined have a band with max. at 300 $\mu\mu$, whilst some specimens show an additional band with max. at 280 $\mu\mu$. The former class have 3 max. in the visible, at ~ 480 , 510, and 590 $\mu\mu$, whilst the latter have additional max. at 540 and 550 $\mu\mu$ ascribed to Yb^{++} as impurity. The decay of luminescence in photochemically discoloured specimens at 20° and 180° follows a hyperbolic law in agreement with a bimol. process. L. J. J.

Luminescence of [barium] platinumocyanide. P. Bergsoe (*5 Nordiske Kemikermode*, 1939, 193—194).—0.1% of Ni completely inhibits the fluorescence of $\text{BaPt}(\text{CN})_6$ (I) and other Pt complexes; Pd is inactive. The apparent existence of yellow and green forms of (I) (A., 1908, i, 252) is due to partial quenching of the fluorescence by ~ 1 p.p.m. of Ni in acid solution. Highly pure (I) has been prepared. M. H. M. A.

Depolarisation of Raman lines. A simplified method. G. Glockler and H. T. Baker (*J. Chem. Physics*, 1943, **11**, 446—449).—Two "Polaroid" films followed by two half-wave mica plates in series are placed at the front of the spectrograph slit, so that the initially mutually perpendicular electric vectors of the radiation are oriented to vibrate in the same direction on striking the prism faces, eliminating differential reflexion. L. J. J.

Raman spectra of acetylenes. VII. Symmetrical-top acetylenes. F. F. Cleveland and M. J. Murray (*J. Chem. Physics*, 1943, **11**, 450—454).—Raman frequencies, relative intensities, and depolaris-

ation factors are recorded for CMe_2Cl , CMe_2CBr , CMe_2CCl , and CBu^tCH . Frequency assignments to different vibration types and calc. C_∞ vals. for 1 atm. in the ideal gaseous state are given for the two first-named. Resonance splitting of the triple-bond fundamental may be due to (2900—700) and (1375+700) cm^{-1} combination frequencies in disubstituted acetylenes. Doubling of the 2100 cm^{-1} fundamental in $\text{OH}\cdot\text{CMe}_2\text{C}\cdot\text{CH}$ and CBu^tCH may be due to the second overtones of highly polarised symmetrical frequencies (~ 700 cm^{-1}) of $\text{C}\cdot\text{CO}\cdot\text{C}$ and $\text{C}(\cdot\text{C})_2$, respectively. L. J. J.

Raman spectra of amino-acids and related compounds. VI. Sarcosine, ethanolamine, choline, betaine, and betaine derivatives. J. T. Edsall (*J. Amer. Chem. Soc.*, 1943, **65**, 1767—1770).—Raman spectra of sarcosine and betaine and their hydrochlorides, phenyl-dimethyl- and pyridine-betaine hydrochloride, choline chloride, $\text{OH}\cdot[\text{CH}_2]_2\cdot\text{NH}_2\cdot\text{HCl}$, and $(\text{CH}_2\cdot\text{NH}_2)_2\cdot 2\text{HCl}$ are reported and correlations between the spectra and structure are indicated. W. R. A.

Conduction of electricity in highly insulating liquids. C. S. Pao (*Physical Rev.*, 1943, [ii], **64**, 60—74).—Investigations on the natural conductivity and on the conductivity induced by γ -rays in *isooctane* and liquid O_2 show characteristics so different as to indicate that the natural conductivity is not due to stray radiation or to cosmic rays. Evidence is given supporting Plumley's theory (cf. A., 1941, I, 319) that the observed conductivity is due to dissociation of the liquid by the field, and against the view that it has a thermionic origin at the cathode, or that it is due to radiation. The relation $\log \text{current} = \text{linear function of (field)}^{\frac{1}{2}}$ is verified. Curves for all data are given. N. M. B.

Molecular compounds of *s*-trinitrobenzene with unsaturated ketones.—See A., 1944, II, 16.

Magnetochemical study of tervalent cobalt complexes. R. W. Asmussen (*5 Nordiske Kemikermode*, 1939, 196—197).—All 6-covalent Co^{+++} complexes are diamagnetic. In the series $[\text{Co}(\text{NH}_3)_6]^{3+}$ (I) $\rightarrow [\text{Co}(\text{NO}_2)_6]^{3+}$ diamagnetic χ falls in each direction to a min. at $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$, while in the series (where known) (I) $\rightarrow [\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (II) vals. of χ are const. $\text{KCo}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$ and $\text{Co}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$ are diamagnetic, and the cation should thus be formulated as (II). M. H. M. A.

Structure of complex aluminium fluorides. C. Brosset (*5 Nordiske Kemikermode*, 1939, 198—199).—Fluoroaluminates are considered as macromols., analogous to the silicates, built up of AlF_6 groups, and showing 3-dimensional (AlF_3) and 2-dimensional (TiAlF_6) networks, chains (Ti_2AlF_8), and simple mols. (Na_3AlF_6). A scheme for representing these types by formulae is presented. M. H. M. A.

Structure of diketene. F. O. Rice and R. Roberts (*J. Amer. Chem. Soc.*, 1943, **65**, 1677—1681).—Liquid diketene (I) was investigated by asepatic distillation, and shown to consist of a single substance. Thermal decomp. in the gas phase gives almost quant. yields of ketene without the formation of free radicals. Hence, according to the principle of least motion, (I) is *cyclobutane-1:3-dione*, although this may not represent the true state of the mol. in the liquid phase. Attention is drawn to the discrepancy between dipole moment data ($\mu = 3.53$) and the present data on the nature of gaseous (I). W. R. A.

Forces between hydrogen molecules. H. Margenau (*Physical Rev.*, 1943, [ii], **64**, 131—147).—Mathematical. By compounding the three types of force involved (exchange, quadrupole, and dispersion) so as to account fundamentally for the size and shape of the mols., a calculation is made of the entire interaction when two H_2 mols. approach. The interaction curves are in fair agreement with empirical curves derived from the second virial coeffs. Quadrupole moments are computed, and the relation between the mol. problem and the corresponding at. problem (interaction between He atoms) is discussed (cf. A., 1940, I, 59). N. M. B.

Partition function for liquids from the harmonic oscillator model. F. A. Matsen and G. M. Watson (*J. Chem. Physics*, 1943, **11**, 343—348).—Mathematical. The energy and frequency of vibration of the mols. of a liquid in their equilibrium positions are expressed in terms of the average intermol. distance by calculating the average potential or spherical symmetry from an assumed force field between pairs of mols. Free vol., ΔH of vaporisation, and the equation of state have been calc. from the resulting potential function. W. R. A.

Relation between surface tension and vapour pressure of liquids and liquid mixtures.—See A., 1943, I, 304.

III.—CRYSTAL STRUCTURE.

Atomic and electronic distributions in liquid nitrogen, nitric oxide, and nitrous oxide. P. C. Sharrah (*J. Chem. Physics*, 1943, **11**, 435—441).—X-Ray diffraction patterns are analysed by the Fourier integral method. Only one pronounced peak is found in each case. Diat. aggregates in liquid O_2 and NO , comparable with gas mols.,

are indicated. The data are consistent with a linear but not with a triangular mol. for N_2O . L. J. J.

Crystal structure of magnesium carbide. M. A. Bredig (*J. Amer. Chem. Soc.*, 1943, **65**, 1482—1483).—It is not possible to ascribe a face-centred tetragonal crystal lattice to MgC_2 , such as that of CaC_2 I, but there is some indication that MgC_2 may be isotypical with the metastable CaC_2 III. W. R. A.

Orientation of Fe_3C crystals in tempered steel. M. Arbusov and G. Kurdjumov (*J. Physics, U.S.S.R.*, 1942, **6**, 163—166).—X-Ray diffraction data for samples of monocryst. austenitic steel containing 1.4% of C, after gradual heating to 600°, show a regular orientation of Fe_3C crystals with respect to the original austenite axes. The [100], [010], and [001] planes of Fe_3C are parallel with the [455], [011], and [522] planes of the austenite, respectively. L. J. J.

Structure of salt hydrates. A. T. Jensen (5 *Nordiske Kemikermode*, 1939, 201—203).—The crystal structure of $SrCl_2 \cdot 6H_2O$ has been determined by successive Fourier approximations. The unit cell (4.105 Å long) contains 1 mol. Each Sr atom is equidistant from 2 other Sr (4.108 Å), and has 6 Cl at 4.90 Å and 6 others at 5.17 Å. The structure is based on chains of the type $-3H_2O-Sr(H_2O)_3-3H_2O-Sr(H_2O)_3-$, the Cl playing a minor part in the stability of the structure. The existence of a centre of symmetry in the crystal suggests that half the chains (statistically distributed) are rotated through 60° with respect to the other half. M. H. M. A.

Configuration of starch in the starch-iodine complex. III. X-Ray diffraction studies on the starch-iodine complex. R. E. Rundle and D. French (*J. Amer. Chem. Soc.*, 1943, **65**, 1707—1710).—From X-ray diffraction, amylose-I complex (I) has a hexagonal unit cell (a_0 12.97, c_0 7.91, d_{100} 11.23 Å) and a helical structure, with a_0 the diameter and c_0 the length of one turn in the helix. These dimensions agree well with a helix consisting of six glucose residues per turn. (I) has been prepared by subjecting amylose in the "V" configuration to I vapour, when one I per 6 glucose residues is absorbed, although this may not be the max. possible absorption. In the "A" and "B" configurations amylose does not absorb I. W. R. A.

Structure of synthetic chain polymers as shown by X-rays. C. S. Fuller and W. O. Baker (*J. Chem. Educ.*, 1943, **20**, 3—10).—X-Ray fibre patterns of polyethylene, polyisobutylene, polyvinyl alcohol, polyvinylidene chloride, several polyesters and polyamides, and cellulose triacetate are reproduced and discussed. L. S. T.

Long X-ray diffraction spacings of the keratins. R. S. Bear (*J. Amer. Chem. Soc.*, 1943, **65**, 1784—1785).—X-Ray diffraction of porcupine quill (α -) and feather (β -)keratins establishes fibre-axis periods of 198 and 95 Å. W. R. A.

Ferritin. V. X-Ray diffraction data on ferritin and apoferritin. I. Fankuchen (*J. Biol. Chem.*, 1943, **150**, 57—59; cf. A., 1943, II, 146).—X-Ray diffraction data show that ferritin (I) and apoferritin crystallise in face-centred cubes of identical cell size, and contain the same protein; the powder X-radiograms differ in line intensities. The packing of the mols. is not disturbed by the introduction of Fe in (I), the Fe atoms apparently occupying interstices between protein mols. R. L. E.

Molecular structure determination by electron diffraction. O. Hassel (5 *Nordiske Kemikermode*, 1939, 113—118).—A review. M. H. M. A.

Electron diffraction. G. P. Thomson (*J. Inst. Metals*, 1943, **69**, 191—199).—A lecture. The val. of electron diffraction methods in studying the nature of polish on metals, the orientation of oil mols. during boundary lubrication, and the structure and orientation of crystals deposited on other crystal surfaces and of compounds formed in the solid state by chemical action on cryst. solids, is discussed. A. R. P.

Structure of the trimeride of phosphonitrile chloride, $P_3N_3Cl_6$. L. O. Brockway and W. M. Bright (*J. Amer. Chem. Soc.*, 1943, **65**, 1551—1554).—Electron diffraction investigation of $P_3N_3Cl_6$ vapour supports a hexagonal ring with P and N alternately and Cl_2 attached in pairs to P atoms. The following vals. are given: P—N 1.65 ± 0.03; P—Cl 1.97 ± 0.03 Å; angle Cl—P—Cl 107—110°. W. R. A.

Electron diffraction investigation of diphenylene. J. Waser and V. Schomaker (*J. Amer. Chem. Soc.*, 1943, **65**, 1451—1455).—Electron diffraction investigations substantiate Lothrop's formula (annexed) with the C—C distance in the hexagonal ring 1.41 ± 0.02 Å, the C—C distance (marked a) 1.46 ± 0.05 Å, the C—H (assumed) 1.10 Å, and a $121 \pm 3^\circ$. Preliminary crystal structure investigations indicate a monoclinic unit cell containing 8 mols., space-group probably $C_{2h}-P2_1/a$. Quantum-mechanical calculations of the resonance energy and relative bond strengths are given. W. R. A.

Rotation of molecules and ions in crystals. C. Finbak (5 *Nordiske Kemikermode*, 1939, 177—183).—A review. M. H. M. A.

Propagation of order in crystal lattices. J. Ashkin and W. E. Lamb, jun. (*Physical Rev.*, 1943, [ii], **64**, 169—178).—Mathematical. Zernike's problem of the propagation of order in a binary crystal alloy is discussed by a matrix formalism of co-operative phenomena. Results are compared with available theoretical treatment. The problem is generalised and cases of more complicated configurations are examined. N. M. B.

Statistics of two-dimensional lattices with four components. J. Ashkin and E. Teller (*Physical Rev.*, 1943, [ii], **64**, 178—184; cf. Kramers, A., 1941, I, 451).—Mathematical. Consideration of a two-dimensional square lattice containing four kinds of atoms, and assuming distinct potential energies of interaction between like and between unlike atoms, shows that where like atoms attract a simple "reciprocity" relation exists between the partition functions at "reciprocally" related pairs of temp. This relation enables a prediction of the nature of the transition point (only one being assumed) to be made and the Curie temp. to be located. The reciprocity relation for attraction between like atoms is found to be invalid for attraction between unlike atoms. N. M. B.

Theory of magnetisation and hysteresis curves of polycrystalline ferromagnetics. E. Kondorski (*J. Physics, U.S.S.R.*, 1942, **6**, 93—110).—A polycryst. ferromagnetic substance consisting of a set of regions with one direction of easy magnetisation is considered. The hysteresis loop for the elementary regions is assumed to be bounded by straight lines. A relation between the magnetisation and the field strength, involving the angular dispersion of the regional axes, is obtained. In the case of randomly distributed axes the consequences of the theory are compared with experimental results for Co, Fe, steel, and permalloy in weak magnetic fields. H. J. W.

Magnetic rotatory power of crystalline nickel sulphate in the short infra-red spectrum. S. Breen, J. N. Humphrey, and L. R. Ingersoll (*Physical Rev.*, 1943, [ii], **64**, 75—77).—Measurements on thin crystals of the α -hexahydrate by the spectro-radiometric method in the range 0.7—1.9 μ . at room temp. and at -125° give curves showing marked anomalies in the dispersion of the rotation at $\sim 0.69 \mu$. and at 1.16 μ , corresponding with those found in the optical rotation for these $\lambda\lambda$. The ratio of the rotation at low and room temp. itself gives an anomalous curve. The effects can be qualitatively explained on the basis of the inverse Zeeman effect. N. M. B.

Adiabatic demagnetisation of iron alum. J. A. Sauer (*Physical Rev.*, 1943, [ii], **64**, 94—112).—Mathematical. The effect, near 0° K., on the magnetic moment and entropy, of perturbations due to cryst. field and magnetic dipole-dipole coupling is calc. exactly to second-order terms in the magnetic coupling and to third-order terms in the cryst. potential. Theoretical vals. of the adiabatic moment agree with available experimental vals. A true thermodynamic scale is established, enabling the temp. to be calc. at any val. of the magnetic field during demagnetisation. The relation of this scale to the temp. determined by the magnetic method is discussed. N. M. B.

Anomalous dependence of the resistance of zinc in a magnetic field. N. M. Nachimovitch (*J. Physics, U.S.S.R.*, 1942, **6**, 111—113).—The resistance of a single Zn crystal at 1.5° and 4.2° K. as a function of the strength of a transverse magnetic field shows anomalies at $H = 10^4$ and 2×10^4 gauss. The effect is similar to that observed by de Haas *et al.* in single Bi crystals (cf. A., 1936, 18). H. J. W.

Frequency spectrum of crystalline solids. II. General theory and applications to simple cubic lattices. E. W. Montroll (*J. Chem. Physics*, 1943, **11**, 481—495; cf. A., 1942, I, 260).—The Born-Karman model is used as the basis for methods of calculation of the frequency spectrum and thermodynamic functions of cryst. solids not very close to their m.p., by means of moments found from traces of powers of a matrix. A simple cubic lattice has a spectrum with two max., near its middle and high-frequency end. The height of the former increases and that of the latter decreases with increasing interaction between next nearest neighbours relative to that between nearest neighbours. Sp. heats are calc. L. J. J.

Slip and twinning in magnesium single crystals at elevated temperatures. P. W. Bakarian and C. H. Mathewson (*Amer. Inst. Min. Met. Eng., Tech. Publ.* 1961, 1943, 28 pp.; *Met. Tech.*, 10, No. 3).—Single crystals of Mg were made by Bridgman's method from metal melted in vac. and cast in H_2 . Specimens cut in numerous crystal orientations were compressed under various stresses at atm. temp. to 340°, and the mechanism of plastic deformation was studied by X-ray and microscopical analyses. Tensile tests were also made on specimens formed by attack with aq. 25% HCl solution, which produced a highly polished surface. The only methods of deformation observed were by slip on the basal plane of the original crystal, twinning on the {102} plane, slip on the basal plane of twinned regions, and cleavage on the {101} plane. Shock-compression tests did not cause the {101} twin formation reported by Schiebold and Siebel (A., 1931, 898). Tension tests showed that the slip direction on {001} or {101} is along the first-order digonal axis in the plane of slip. The {101} slip bands are irregular, resembling those found

in α -Fe, and slip bands in twin and parent crystal matched. Sublimation pits formed at high temp. followed slip bands and sometimes twin boundaries. J. C. C.

Directional characteristics of single-texture-structure copper strip. M. Cook and T. L. Richards (*J. Inst. Metals*, 1943, 69, 201—207).—The resolved shear stress on the slip planes in slip directions has been calc. in terms of the applied stress in various directions for Cu strip with a single-texture structure resembling that of a single crystal. The strip, which had been cold-rolled to 95% reduction and annealed for 1 hr. at 550°, showed a max. tensile strength, and elongation at 45° to the direction of rolling, and min. tensile strength at 22.5° and 67.5° thereto. The resolved shear stress on the operating slip planes required to cause fracture is const. for all directions of test-piece except the 0° and 90° directions, in which the elongation is a min.; cups made with strip having a single texture show pronounced ears also in these directions. A. R. P.

Pressure effect on linear rate of crystallisation of silicates. M. P. Volarovitch and A. A. Leontieva (*J. Phys. Chem. Russ.*, 1943, 17, 45—50).—The rate (v) of crystal growth of $\text{Na}_2\text{Si}_2\text{O}_6$ in a glass containing SiO_2 73.3, Na_2O 26.7 wt.-% is max. at 760°. Max. v increases from 1.2×10^{-5} at 1 kg. per sq. cm. to 9.3×10^{-5} cm. per sec. at 700 kg. per sq. cm. As the pressure on the glass was transferred by compressed N_2 , N_2 may be the cause of the increase in v . More probably η of glass is lowered by pressure; the rate of bending of a horizontal glass fibre supported at its ends is at 325 kg. per sq. cm. ~ 30 times that at 1 kg. per sq. cm., both at 500—550°. J. J. B.

Cohesion of solid benzene at its m.p. G. Bruni (*Kolloid-Z.*, 1943, 103, 60—61).—The tensile strength of plates of solid C_6H_6 at its m.p., prepared as free as possible from fissures, was found to be 14.5 kg. per sq. cm., and the breaking length 143.28 m.

R. H. F.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Mol. wt. of solid benzene derived from its cohesion. G. Bruni (*Kolloid-Z.*, 1943, 103, 61—65; see above).—The author's general equation of state is applied to solid C_6H_6 at its triple point. The mol. wt. calc. from it, using the experimental val. for the cohesion, corresponds with $(\text{C}_6\text{H}_6)_{18}$, exactly one ninth of the val. at the crit. point, $(\text{C}_6\text{H}_6)_{182}$. Some significance is attached to the factor 9, and the existence of a sub-unit of the H atom of at. wt. one ninth is postulated. R. H. F.

Relation between m.p. and mol. wt. of paraffins.—See B., 1943, I, 480.

Viscosity and mol. wt. of solutions of cellulose and its derivatives.—See B., 1943, II, 373.

Electrical conductivity and isothermal Hall effect in cuprous oxide. W. Feldman (*Physical Rev.*, 1943, [ii], 64, 113—118).—Investigations from room temp. to 700° show that at the higher temp. the conductivity is represented by $\sigma = Ae^{-E/kT}$, but that below 300° the exponential law is not obeyed. The max. and min. of the σ curves in the latter region are presumed to result from a combination of a saturation of clusters and a rapid decrease of mobility with temp. Hall effect measurements up to 450° show that the no. of current carriers does not obey the exponential law of temp.-dependence. An anomaly in the mobility is observed at $\sim 150^\circ$ where the mobility changes from a T^{-2} to a T^{-1} dependence. N. M. B.

Effect of high electrostatic fields on the conductivity of tungsten. P. L. Vissat (*Physical Rev.*, 1943, [ii], 64, 119—125).—Measurements on a W wire 0.0078 mm. diameter in vac. with fields of $\sim 10^6$ v. per cm. showed that an increase in resistance always resulted from application of the field, the change was different for different temp. of the filament and variations of vac., no measurable change resulted unless the field exceeded a certain val., and a small leakage or ionisation current was associated with the changes in resistance. Calculations show that results are wholly explained by ionisation currents if it is assumed that most of the ionisation occurs near the surface of the wire. N. M. B.

Magnetic moment of superconductors. I. E. Nachutin (*J. Physics, U.S.S.R.*, 1942, 6, 114—115).—The magnetic moment of a single-crystal sphere of Sn at 2.59° K. for fields up to the crit. val. was measured. No significant difference between the behaviour in fields parallel to the tetrad axis and to one of the diad axes was detected. H. J. W.

Magnetic susceptibility of oxygen and nitric oxide at low field strengths. A. Burris and C. D. Hause (*J. Chem. Physics*, 1943, 11, 442—446).—Measurements of mass susceptibility with a Rankine magnetic balance at 1 atm. and ~ 15 oersteds give vals. of $106.3 \pm 0.2 \times 10^{-6}$ for O_2 and 47.2×10^{-6} for NO. For O_2 , χ_{calc} is 0.997 ± 0.002 , and for NO the vol. susceptibility is 0.0590×10^{-6} . The mass susceptibility of H_2O at 20° is taken as -0.7200×10^{-6} . L. J. J.

Magnetochemical studies. XL. Magnetic behaviour of uranium and uranium tetrachloride. H. Bommer (*Z. anorg. Chem.*, 1941, 247,

249—258).—The susceptibility (χ) of Fe-free U was measured between 90° and 488° K. χ is independent of the field strength between 195° and 488° K. U is paramagnetic, but the $1/\chi_{\text{at}}-T$ graph is not linear. χ_{at} at room temp. = $+620 \times 10^{-6}$. The Th-U series does not conform with the earlier rules for the magnetic behaviour of transition elements. UCl_4 , above room temp., obeys the Curie-Weiss law with $\theta +50^\circ$. The moment is 2.7 Bohr magnetons. Below room temp. at. binding occurs. J. F. H.

Specific heat ratios in carbon dioxide. L. Katz (*J. Chem. Physics*, 1943, 11, 496—497).—A no. of published vals. of γ for CO_2 when reduced to zero pressure are $>$ vals. calc. from spectroscopic data. L. J. J.

Heat contents at high temperatures of the anhydrous chlorides of calcium, iron, magnesium, and manganese. G. E. Moore (*J. Amer. Chem. Soc.*, 1943, 65, 1700—1703).—Vals. of heat contents from room temp. to 1670° K. have been determined for anhyd. CaCl_2 , FeCl_2 , MgCl_2 , and MnCl_2 . Vals. of m.p. and heats of fusion (g.-cal. per g.-formula wt.) are: 1055° , 6780 ± 80 ; 950° , $10,280 \pm 50$; 987° , $10,300 \pm 50$; 923° , 9000 ± 50 . Heat content and entropy increments are tabulated at 100° intervals from 400° to 1700° K. W. R. A.

Thermal data. XVII. Heat capacity, entropy, and free energy of formation of cyclohexane. New method of heat transfer in low-temperature calorimetry. R. A. Ruehrwein and H. M. Huffman (*J. Amer. Chem. Soc.*, 1943, 65, 1620—1625).—Vals. of C_p from 13° to 301° K. were measured calorimetrically in an apparatus (described) involving a new method of heat transfer by mechanical contact. Vals. of heat of transition, heat of fusion, and entropy and free energy at 298.16° K. are: 1610.8 ± 0.4 ; 639.8 ± 0.3 g.-cal. per mol.; 48.84 g.-cal. per degree per mol.; 5.99 kg.-cal. per mol. (See also C., 1944, Part I.) W. R. A.

Triple point of water. W. Waring (*Science*, 1943, 97, 221—222).—The triple point is at $+0.0098^\circ$ and not at $+0.0074^\circ$ as usually given. Inconsistencies in v.p. vals. for ice and water near 0° are pointed out. E. R. R.

Relation between d_{15}^{15} and d_{15}^{20} for petroleum products.—See B., 1943, I, 479.

Vapour pressure curves for normal H and D compounds. K. Stokland (5 *Nordiske Kemikermøde*, 1939, 204—205).—V.p. curves have been determined for $\text{Si}_n\text{H}_{2n+2}$ and $\text{Si}_n\text{D}_{2n+2}$ ($n = 1-4$) from 1 to 760 mm. Hg. When $n = 1$, the H compound has higher v.p. only below ~ 100 mm. Hg. and when $n = 2, 3$, or 4 the D compounds have higher v.p. throughout, thus disproving Clusius' rules (A., 1938, I, 129). M. H. M. A.

Determination of orthobaric curve and critical density and temperature with data for ethylene [di]chloride and boron tribromide. K. Hojendahl (5 *Nordiske Kemikermøde*, 1939, 209—211).—Varying amounts of the material are sealed (air-free) into ampoules (8 cm. long, 4 mm. diameter); these are heated inside a Cu cylinder, and the temp. of disappearance of the meniscus is observed by the disappearance of a luminous reflected image. BBr_3 has $T_c = 300^\circ \pm 2^\circ$, $D_c = 0.9$; $\text{C}_2\text{H}_4\text{Cl}_2$ has $T_c = 290^\circ \pm 2^\circ$, $D_c = 0.45$. M. H. M. A.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Statistical mechanics of binary mixtures. T. Alfrey and H. Mark (*J. Chem. Physics*, 1943, 11, 496).—A reply to Kottler (A., 1943, I, 179). L. J. J.

Specific heats of mixed acids at higher temperatures. J. J. Morgan, D. A. Bender, and R. G. Capell (*Chem. Met. Eng.*, 1943, 50, No. 6, 122—124).—Determinations of sp. heats of mixtures of HNO_3 and H_2SO_4 are reported for 40°, 60°, 80°, and 100° and triangular plots are given. For these temp. the change of sp. heat with temp. is small. H. W. T.

Conception of osmotic pressure. A. Thiel (*Kolloid-Z.*, 1940, 91, 316—318).—An answer to Metcalf's criticisms (A., 1940, I, 354) of the author's theory of osmosis (*ibid.*, 316) and a criticism of Metcalf's theory. J. H. Ba.

Determination of ionic weights by the dialysis method. II. Sources of error in the method. A. von Kiss and V. Acs (*Z. anorg. Chem.*, 1941, 247, 190—204).—In solutions containing a foreign electrolyte in sufficient concn. the relation $\lambda/\sqrt{M} = \lambda_\infty/\sqrt{M_\infty} = \text{const.}$ (I) holds; M and M_∞ are the wts. and λ and λ_∞ are the dialysis coeffs. of the reference and unknown ions respectively. For free diffusion Riecke's law, $D_1/\sqrt{M_1} = D_2/\sqrt{M_2} = \text{const.}$ is only approx. true. Only ions with approx. equal wts. and similar structure can be compared. The external, "physical" hydration of the ions hinders diffusion and may lead to invalidity of equation (I). It is doubtful whether reliable hydration nos. can be obtained from the dialysis method. The various effects of complex formation may cause invalidity or indeterminateness of (I). The variable results obtained with different membranes show that narrow-pored membranes are unsuitable. It was shown experimentally that Cello-

phane and Cuprophane are unsuitable but that Cellafilter gives good constancy for $\lambda_s/\sqrt{M_s}$. J. F. H.

Alloys of magnesium. XIV. Constitution of the magnesium-rich alloys of magnesium and manganese. J. D. Grogan and J. L. Haughton (*J. Inst. Metals*, 1943, 69, 241—248).—Alloys with up to 5% Mn were prepared by reaction of a large mass of molten Mg with anhyd. MnCl_2 and the liquidus of the system was then determined by analysing dip samples taken at definite temp. above the eutectic (651°, 2% Mn). The results showed the liquidus to be almost linear between the eutectic temp. and 850°, 7% Mn. From 0 to 2% Mn the liquidus lies very close to the solidus. The solid solubility of Mn in Mg decreases rapidly from ~2% at 650° to <0.5% at 450°.

A. R. P.

Constitution of magnesium-manganese-zinc-aluminium alloys in the range 0–5% Mg, 0–2% Mn, 0–8% Zn. I. The liquidus. E. Butchers, G. V. Raynor, and W. Hume-Rothery. **II. Composition of the MnAl_6 phase.** G. V. Raynor and W. Hume-Rothery. **III. The 500° and 400° isothermals.** A. T. Little, G. V. Raynor, and W. Hume-Rothery (*J. Inst. Metals*, 1943, 69, 209—228, 415—421, 423—440).—I. Liquidus curves have been determined accurately for the systems Mg–Al and Zn–Al, and liquidus surfaces for the systems Mg–Zn–Al, Mg–Mn–Al, Mn–Zn–Al, and Mg–Mn–Zn–Al in the Al-rich region. Alloys containing Mn are of two classes in one of which MnAl_6 and in the other α -Al-rich solution is primary. Equations are given for all the curves and surfaces of primary crystallisation and for the binary eutectic surface in the quaternary system. The f.p. depression in the Mg–Zn–Al system is slightly < would be expected from a purely additive relation based on the liquidus curves of the binary systems.

II. From slowly cooled Mn–Al alloys with and without Mg or Zn or both, needles of MnAl_6 were isolated by anodic dissolution of the Al in 2N-HCl or 2N- HNO_3 , and examined by X-rays and chemical analysis. The composition MnAl_6 was confirmed. No Mg was dissolved by the compound when the alloy contained Mg, but a small amount (>0.4%) of Zn was dissolved when the alloy contained up to 8% Zn.

III. At 500° Al dissolves about 0.35% Mn, but additions of Mg or Zn reduce this val. to <0.1% with 4% Mg or 2% Zn. In the quaternary system the totally solid region at 500° is bounded by a vertical surface such that % Mg = $12 - 1.32 \times (\% \text{ Zn}) + 0.052 \times (\% \text{ Zn})^2$, and the homogeneous α -field by a surface such that % Mn = $1/[0.6 \times (\% \text{ Mg}) + 0.8 \times (\% \text{ Zn}) + 0.55 \sqrt{(\% \text{ Mg} \times \% \text{ Zn})}] + 1.667]^2$. Alloys with more Mn than that calc. from the second equation contain MnAl_6 with or without a small amount of liquid according to the % of Zn and Mg. At 400° the amount of Mn retained in solid solution is negligible, all the alloys containing MnAl_6 needles. In the Zn–Mg–Al system within the range studied the alloys consist of α or $\alpha + \text{Al}_2\text{Mg}_3\text{Zn}_3$, the boundary between the two fields being given by $(\text{at.}\% \text{ Zn})/(\text{at.}\% \text{ Mg}) = K$; this expression also holds for lower temp. with other vals. of K such that $d \log K/dT = -Q/RT^2$. In the quaternary system the alloys are of the $\alpha + \text{MnAl}_6$ or $\alpha + \text{MnAl}_6 + \text{Al}_2\text{Mg}_3\text{Zn}_3$ type; methods of calculating the boundary between the two fields are described.

A. R. P.

Constitution of alloys of aluminium with manganese, silicon, and iron. I. Binary system aluminium-manganese. II. Ternary systems aluminium-manganese-silicon and aluminium-manganese-iron. H. W. L. Phillips. III. Ternary system aluminium-silicon-iron. IV. Quaternary system aluminium-manganese-silicon-iron. H. W. L. Phillips and P. C. Varley (*J. Inst. Metals*, 1943, 69, 275—316, 317—350).—I. The Al–Mn system was investigated by thermal analysis and by micrographic examination of annealed and slowly cooled alloys. On slow cooling Al and MnAl_6 form a eutectic at 2.16–2.2% Mn, 655°, but extrapolation from solubility measurements places the eutectic at 1.9% Mn. Peritectic reactions occur at 680°, liquid + $\text{MnAl}_6 \rightarrow \text{MnAl}_4$; at 822°, δ + liquid $\rightarrow \text{MnAl}_4$; and at 880°, liquid + $\epsilon \rightarrow \delta$. The δ and ϵ phases were not identified. On slow cooling a sheath of reaction product envelops the primary phase and the solid alloys often contain metastable phases; completion of the reactions is obtained only by prolonged annealing just below the peritectic temp. The apparent reliquifaction which occurs on cooling alloys with 25–37% Mn through the range 680–700° is shown to be due to the difference in crystal habit between the primary MnAl_4 above 700° and the MnAl_6 formed peritectically at 680°.

II. The constitution of Al–Mn–Si alloys over the range in which Al is primary was studied as they were slowly cooled. The Al-rich alloys contain at least one of the phases MnAl_6 , Si, and a ternary α -(Mn–Si) phase formed peritectically from MnAl_6 ; there is an invariant point at 649°, Mn 2, Si 1.3% at which MnAl_6 , α -(Mn–Si), and Al are in equilibrium with liquid. α -(Mn–Si) appears to have a variable composition; it forms a ternary eutectic with Si and Al at 573°, Si 11.75, Mn 0.75%. In alloys rich in Mn and Si the primary crystals consist of ternary β -(Mn–Si) which forms a eutectic complex with MnAl_6 , reacts peritectically with liquid to give MnAl_4 or α -(Mn–Si), and has two invariant points in the boundaries of its primary field, (a) at 660°, Mn 3.4, Si 0.5% at which MnAl_6 , β -(Mn–Si), and MnAl_4 are in equilibrium with liquid, and (b) at 658°, Mn 2.7,

Si 1.3% at which MnAl_6 , β -(Mn–Si), and α -(Mn–Si) are in equilibrium with liquid. As in the binary Mn–Al alloys equilibrium is attained in the ternary alloys only after a prolonged high-temp. anneal. In Al-rich alloys a long anneal tends to complete the formation of α -(Mn–Si) from MnAl_6 and hence reduces the amount of free Si in the alloy, an important point in commercial alloys since free Si tends to impart a brown colour to the anodic film. In the Al–Mn–Fe system MnAl_6 , FeAl_3 , and Al form a ternary eutectic at 654°, Mn 0.75, Fe 1.75%. FeAl_3 forms eutectics with both MnAl_6 and MnAl_4 , and can dissolve considerable Mn, whilst both Mn compounds will dissolve Fe. MnAl_6 , MnAl_4 , and FeAl_3 are in equilibrium with liquid at 730°, Fe 3.4, Mn 2.4%. Fe raises the peritectic temp. at which MnAl_6 is formed and causes MnAl_6 to be primary at a lower Mn content of the alloy. On adding Fe to commercial Mn–Al alloys, therefore, the size and no. of the MnAl_6 crystals are increased and then FeAl_3 appears; the crystals of both compounds are broken up on rolling and the particles restrict grain growth on annealing.

III. Earlier work on the constitution of the Al–Si–Fe system has been confirmed except that the liquidus temp. in the primary FeAl_3 field were found to be slightly low owing to undercooling.

IV. The equilibria in the range from pure Al to 4:4:4:88 Fe–Si–Mn–Al alloy have been studied in detail. No quaternary compounds were found; α -(Fe–Si) and α -(Mn–Si) form a continuous series of solid solutions and there are six primary regions due to Al, FeAl_3 , MnAl_4 , MnAl_6 , β -(Mn–Si), and α . Al forms binary eutectic surfaces with FeAl_3 , MnAl_6 , α , β -(Fe–Si), and Si; FeAl_3 forms similar surfaces with MnAl_4 , MnAl_6 , and β -(Mn–Si). The various peritectic reactions in the system rarely proceed to completion, envelopment frequently occurring and causing the persistence of many metastable constituents; undercooling and unsaturation of the solid phases often prevent attainment of equilibrium. Quaternary invariant points occur at (a) 731°, Mn 3.85, Si 0.35, Fe 2.35%, between liquid, MnAl_4 , FeAl_3 , β -(Mn–Si), and MnAl_6 ; (b) 695°, Mn 2.60, Si 1.35, Fe 2.35%, between liquid, FeAl_3 , β -(Mn–Si), MnAl_6 , and α ; (c) 648°, Mn 0.35, Si 1.75, Fe 2.00%, between liquid, FeAl_3 , MnAl_6 , α , and Al; (d) 575°, Mn 0.2, Si 11.7, Fe 0.6%, between liquid, α , β -(Fe–Si), Al, and Si. Final solidification of all the alloys occurs at the Al– α -Si or the Al– β -(Fe–Si)–Si ternary eutectic according to the composition and the rate of diffusion of Fe into the solid phases in the early stages of solidification. In commercial Mn–Al alloys with incidental Fe and Si impurities a small amount of Mn is taken into solid solution by Al or FeAl_3 , the remainder occurring as MnAl_6 or associated with Fe and Si as α . The Si is partly in solution in the Al, partly combined as α - or β -(Fe–Si), and partly as free Si. Fe occurs as FeAl_3 , dissolved in MnAl_6 , or combined as α - or β -(Fe–Si). Hot-working or annealing tends to complete the peritectic reactions involving the formation of α from MnAl_6 or FeAl_3 and thus leads to reduction in the amount of free Si.

A. R. P.

Constitution of the iron-rich iron-nickel-silicon alloys at 600°. E. S. Greiner and E. R. Jette (*Amer. Inst. Min. Met. Eng.*, 1943, *Tech. Publ.* 1573, 16 pp.; *Met. Tech.*, 10, No. 3).—This investigation was carried out by X-ray diffraction methods on homogenised powdered samples quenched from ~600°. In a ternary plot, the body-centred cubic α phase is bounded by four two-phase areas separated by three three-phase areas. Three of the phases correspond in structure to similar phases in the binary Fe–Ni or Fe–Si alloys; two are new phases: λ , a cubic structure with an edge length of 6.131 Å, and ϵ , a tetragonal structure with a 8.308 Å, and c 9.012 Å. The solid solubility of Ni in the α phase changes from 3.5 at.% in Fe–Ni alloys to 13.6 at.% in ternary alloys containing 22.4 at.% of Si.

J. C. C.

Hardness of certain primary copper solid solutions. J. H. Frye, jun., and K. W. Caum (*Amer. Inst. Min. Met. Eng.*, 1943, *Tech. Publ.* 1564, 8 pp.; *Met. Tech.*, 10, No. 2).—Meyer hardness analyses were carried out on alloys of Cu with >5% of Ge, Ga, Zn, and As, the tests being made on worked and annealed vac.-melted samples having a grain diameter of 0.074 mm. For a given at.% of each solute, the Meyer hardness vals. P_s and P_a were \propto the calc. expansion of the Cu lattice.

J. C. C.

Hardness and lattice stress in solid solutions. J. H. Frye, jun., J. W. Caum, and R. M. Treco (*Amer. Inst. Min. Met. Eng.*, 1943, *Tech. Publ.* 1572, 7 pp.; *Met. Tech.*, 10, No. 3).—There is a single, simple relation between the increase in hardness and the increase in lattice stress when Zn dissolved in Cu is replaced by Ga, Ge, or As and when Cd in Ag is replaced by In, Sn, or Sb. In these relations, the overlap of the electron clouds of the ions as a possible factor additional to the lattice parameter in determining hardness is eliminated.

J. C. C.

Ageing in the solid solution of silver in aluminium. A. H. Geisler, C. S. Barrett, and R. F. Mehl (*Amer. Inst. Min. Met. Eng.*, 1943, *Tech. Publ.* 1557, 20 pp.; *Met. Tech.*, 10, No. 2).—X-Ray diffraction studies of Al alloys containing 10, 20, and 30% of Ag aged at 158–303° indicate that ageing is accompanied by pptn. of a transformation lattice γ' in thin plate-like particles which later transform into the equilibrium phase γ . The matrix planes along which the

platelets are formed can be determined from central radial streaks in Laue photographs. Microscopical examinations show that the γ - γ transformation is accompanied by a hitherto unobserved discontinuous type of reaction nucleated at the grain boundaries and probably involving recrystallisation of the strained matrix. The mechanism of hardening is discussed; in these alloys the chief factors may be the pptn. of γ and the stresses involved in keeping the equilibrium phase in this strained condition. J. C. C.

Thermodynamical theory of restoration phenomena in the ageing of copper-aluminium alloys. S. T. Konobeevski (*J. Inst. Metals*, 1943, 69, 397—413).—In the ageing of Cu-Al alloys the CuAl_2 phase is pptd. in thin plates and, owing to its high degree of dispersion, can exist in metastable equilibrium in slightly supersaturated solution; when the temp. is raised the ppt. redissolves, thus producing the "restoration" observed when naturally aged duralumin is heated. From the temp. at which restoration is completed the relative amount of the pptd. phase may be calc. as a function of the temp. and total alloy concn. The dimensions of the equilibrium nuclei are independent of the total alloy concn. but the no. of pptd. crystals depends on the initial concn. of the solid solution since this determines the crit. magnitude of the nucleus and hence the energy of formation of the phase. If the no. of grains formed depends exponentially on their energy the magnitude of the pptd. crystals and the surface energy of the boundary between the pptd. phase and the solid solution can be estimated. On this theory the dimensions of the equilibrium crystal of CuAl_2 formed during room-temp. ageing of Cu-Al alloys are diameter $\sim 10^{-7}$ cm. and thickness $\sim 3 \times 10^{-8}$ cm., vals. which agree closely with those found experimentally by other workers. In the 5% Cu-Al alloy the no. of pptd. crystals is 1.3×10^{10} per g. and in the 2% Cu alloy 0.5×10^{10} per g. The sp. surface energy is 0.75×10^{-5} g.-cal. per g. A. R. P.

Effects of precipitation treatment of binary magnesium-aluminium alloys. F. A. Fox and E. Lardner (*J. Inst. Metals*, 1943, 69, 373—396).—The structures produced by pptn. of β from supersaturated solid solutions of Al in Mg depend on the Al content, the pptn. temp., and, to a smaller extent, the time. At any temp. the ppt. first forms at the grain boundaries and then, at $<200^\circ$, grows into the grains in the form of closed waves producing a pearlitic structure; in large-grained alloys a mosaic type of pptn. appears soon after pearlite begins to form. In alloys with $>8\%$ Al crystallographic osmondite forms, some time after the first appearance of pearlite, in those areas of the grain which are free from the latter, which then ceases to grow. Above 200° coarse sorbitic and pearlitic areas form from the grain boundaries inwards, mosaic outlines appear soon after the sorbite, and these are followed by crystallographic osmondite which rapidly coarsens to granular osmondite. For a given pptn. treatment the finest ppt. and the best mechanical properties of the alloy are obtained with the highest Al contents. A. R. P.

Mechanism of precipitation from solid solutions of zinc in aluminium, magnesium in aluminium, and of some magnesium-base alloys. A. H. Geisler, C. S. Barrett, and R. F. Mehl (*Amer. Inst. Min. Met. Eng.*, 1943, *Tech. Publ.* 1558, 22 pp.; *Met. Tech.*, 10, No. 2).—In Zn-Al alloys, X-ray diffraction, electrical resistivity, and hardness measurements indicate that age-hardening accompanies the formation on the octahedral matrix planes of coherent platelets having a strained lattice of the Zn type. On over-ageing, when softening is observed, the particles grow but break away from the matrix before they are thick enough to diffract as three-dimensional gratings. In Mg-Al alloys, coherent platelets first form on {100} matrix planes and grow to a well-defined Widmanstätten figure, subsequent pptn. occurring on {120} Al planes. Age-hardening occurs during the entire decomp. In Pb-Mg and Sn-Mg alloys, the platelets do not grow very large and hardening is negligible. The results lend support to a modified theory of age-hardening; crit. dispersion is not sufficient in itself to explain hardening, but it is necessary that the matrix and the ppt. should be closely related in orientation. Hardening is \propto the size to which these coherent particles may grow before breaking away from the matrix. J. C. C.

Electrical properties of copper-manganese-aluminium alloys. M. Cook and W. O. Alexander (*Trans. Faraday Soc.*, 1943, 39, 260—265).—The sp. resistance and temp. coeff. of resistance have been measured for 4 binary and 4 ternary alloys containing Cu 88.0—95.5%, Mn 5—10%, Al 1—5.5%, in the form of wire, hard drawn and annealed at 600° , over the range 0— 350° . The tensile strength, elongation, and coeff. of thermal expansion were also determined. Alloys with $\leq 2\%$ of Al do not scale at temp. $<600^\circ$. F. L. U.

Magnetic behaviour of superconducting tin-zinc alloys. B. G. Lazarev and I. E. Nachutin (*J. Physics, U.S.S.R.*, 1942, 6, 116—119).—Sn-Zn alloys containing 90%, 34%, and 10% of Sn and pure Sn were used. The crit. magnetic field is the same function of the temp. (between 2.64° and 3.72° K.) for all of these. In weak fields the magnetic behaviour of all the samples was identical, but in stronger fields the hysteresis increased with the proportion of Zn in the alloy. It is suggested that magnetic screening of the

Zn by superconducting grains of Sn and the formation of closed superconducting circuits are possible explanations of the observed effects. H. J. W.

Solubility of salts in aqueous carbamide solutions. K. J. Pedersen (5 *Nordiske Kemikermode*, 1939, 180—191).—The solubilities of 15 org. and inorg. salts in 0.25—1.0M. aq. $\text{CO}(\text{NH}_2)_2$ at 18° have been determined (cf. A., 1939, I, 195). $\text{Na}_2\text{C}_2\text{O}_4$ had a smaller solubility than in H_2O , but all the others showed increases, $\alpha - (s - s_0)/cs$ being almost independent of c . Vals. for α were in rough agreement with the theory that the increased solubilities are due partly to increased I and partly to increased ϵ . M. H. M. A.

Solubility of potassium iodide in potassium hydroxide solutions at 20° . H. D. Kirschman and R. Pomeroy (*J. Amer. Chem. Soc.*, 1943, 65, 1695—1696).—Solubility and ρ of KI in 0—14.35N-KOH (1% K_2CO_3) at 20° have been determined. The curves show no discontinuities. W. R. A.

Electrical conductivities of salts and solubilities of barium sulphate in water-ethyl alcohol solutions.—See A., 1944, I, 18.

Solubility and dissociation of cryolite in aqueous [salt] solutions. H. Buchwald (5 *Nordiske Kemikermode*, 1939, 259—260).—The solubility of Na_3AlF_6 (I) in H_2O (0— 95°) and dil. HCl, HF, NaCl, and NaF solutions (25°) has been determined. The solubility decreases with increasing $[\text{Na}^+]$, $[\text{F}^-]$, and pH, but is unaffected by change in $[\text{Cl}^-]$. The pH of saturated (I) solution in dil. HCl is $>$ theoretical and agrees with the complete dissociation: $(\text{I}) \rightarrow 3\text{Na}^+ + \text{AlF}_6^{3-} + 2\text{F}^-$ ($\text{H}^+ + \text{F}^- \rightarrow \text{HF}$), As $K_8 = ([\text{Na}^+]^3 [\text{AlF}_6^{3-}] [\text{F}^-]^2)$ is nearly const. ($\sim 2.7 \times 10^{-16}$) in all the above solutions it is concluded that this dissociation of (I) always occurs. M. H. M. A.

Solubilities of high mol. wt. symmetrical normal aliphatic ketones. F. M. Garland, C. W. Hoerr, W. O. Pool, and A. W. Ralston (*J. Org. Chem.*, 1943, 8, 344—357).—Solubilities of COR_2 ($\text{R} = n\text{-C}_6\text{H}_{13}$, $\text{-C}_8\text{H}_{17}$, $\text{-C}_{10}\text{H}_{21}$, $\text{-C}_{12}\text{H}_{25}$, $\text{-C}_{14}\text{H}_{29}$, and $\text{-C}_{16}\text{H}_{33}$) in C_6H_6 , cyclohexane, CCl_4 , EtOAc , BuOAc , COMe_2 , COMeEt , MeOH , 95% EtOH , Pr^iOH , Bu^iOH , EtNO_2 , and MeCN at, usually, ~ 10 — $\sim 80^\circ$, are recorded. R. S. C.

Photoactivation of crystals. G. Cohn (5 *Nordiske Kemikermode*, 1939, 192).—The adsorptive power of ZnS and CdS (I) phosphors for dyes is increased by illumination, but of (I) for phenolphthalein is decreased by illumination with light unabsorbed by (I). (Cf. A., 1939, I, 561.) M. H. M. A.

Adsorption of vapours on carbonised coal.—See B., 1943, I, 477.

Surface tension of white phosphorus. E. Hutchinson (*Trans. Faraday Soc.*, 1943, 39, 220—234).—The surface tension of white P has been measured by the max. bubble pressure method with CO_2 over the range 50.0 — 68.7° . The respective vals. of γ at these temp. are 69.70 and 64.95 ± 0.3 dynes per cm. The val. of the at. parachor of P in compounds is intermediate between those calc. from these results for ring structures P_4 and P_8 . The Eotvos const. is 1.38. A method for measuring interfacial tensions modelled on Sugden's max. bubble pressure method is described, and measurements are recorded for the tension of molten P against H_2O , C_6H_6 , cyclohexane, $n\text{-C}_8\text{H}_{18}$, EtOH , and COMe_2 . F. L. U.

Surface energy and heat of vaporisation. H. Dunken, H. Klapproth, and K. L. Wolf (*Kolloid-Z.*, 1940, 91, 232—243).—Stefan's relation between the mol. internal heat of vaporisation L_1 and the total mol. surface energy W_s , viz., $L_1/W_s = \phi = 2$, does not hold in general but depends on the co-ordination no. of the substance in the bulk (z) and in the surface (z_s). In general $\phi = z/(z - z_s)$. Vals. of ϕ are calc. for various lattice structures. For liquids ϕ (varies between 2.2 and 8.3) depends also on the difference in association in the vapour and liquid phases and for non-polar liquids has a val. 2.5—3.5. This indicates spherical symmetry in the mol. packing. Allowing for association in the liquid phase a similar val. of ϕ is obtained for various alcohols. A knowledge of ϕ can be used to assess the degree or heat of association of a liquid. J. H. BA.

Capillary systems. XIX. Capillary back pressure, capillary diameter, and the passage of a phase boundary through a single capillary and capillary systems. (Theoretical). E. Manegold, K. Solf, and E. Albrecht (*Kolloid-Z.*, 1940, 91, 243—275).—Formulæ are derived for the times and pressures of exit, entrance, and bubble formation when a phase boundary passes through a capillary system. Calculations of these quantities are made for certain systems. Knoll's results (A., 1940, I, 273) are analysed in the light of the theory. J. H. BA.

Surface diffusion. H. Wergeland (5 *Nordiske Kemikermode*, 1939, 253).—The probability, S , that an adsorbed mol. will migrate to an adjacent activated point of the adsorbent in time t is given, with certain simplifying assumptions, by: $S \propto \{1 - \Phi(Q/\sqrt{ct})\}$, where Φ = Gaussian integral of error, Q = activation energy, and c = (mean?) variation. M. H. M. A.

Influence of surface films of oil on evaporation of water. R. W. Powell (*Trans. Faraday Soc.*, 1943, 39, 311—318). The rate of vapourisation of H_2O through surface films of oil depends on the diffusion coeffs. and D_0 of H_2O in oil and in air, and on the

effective thickness of the oil and air layers in which diffusion occurs. The thickness of the air diffusion layer has been measured for various air speeds. D_0 , measured for three different oils, increases with the thickness of the oil layer, and for thin films is $\sim 3 \times 10^{-3}$ cm.² per sec. In agreement with previous workers it is concluded that unimol. oil films are ineffective, and that the relative reduction of evaporation increases with the speed of the air current when multimol. films are used. F. L. U.

Optical theory of chromatic emulsions and of the Christiansen experiment. G. N. Ramachandran (*Proc. Indian Acad. Sci.*, 1943, 18, A, 67—79).—The observations of Sethi (*Proc. Indian Assoc. Cult. Sci.*, 1921, 6, 124) and Sogani (A., 1926, 336) can be explained by a theory based on diffraction of light by a sphere immersed in a medium of nearly the same refractive index. Expressions are derived for intensity and spectral character of transmitted and diffracted light. L. J. J.

Electrical conductivity of colloids. T. R. Bolam and A. K. M. Trivedi (*Trans. Faraday Soc.*, 1943, 39, 247—253).—The conductivity of Oden S sols decreases on dilution more rapidly than does the concn. Membrane equilibrium and conductivity data indicate that this is due to interionic action between the adsorbed polythionate ions and their counter-ions, leading to an apparent increase in Λ of the bound polythionate with increase in sol concn. This behaviour supports Hartley's theory (cf. A., 1939, I, 469) of the conductivity of electrolytes of unsymmetrical valency-type. F. L. U.

Development and present position of the theory of filtration of suspensions. A. Brighel-Müller (*Kolloid-Z.*, 1940, 92, 285—299).—A crit. review of the literature. A bibliography is appended. F. L. U.

Silver sol. H. R. Kruyt and H. L. van Nouhuys (*Kolloid-Z.*, 1940, 92, 325—342).—Stable Ag sols are prepared by electrical dispersion in H₂O, dil. NaOH, or saturated aq. AgOH, those made in presence of NaOH ($\sim 10^{-3}$ N) being the most highly disperse and the most stable. In all these sols the stabilising ion is AgO'. Dispersion in an atm. of O₂-free H₂ or N₂ does not affect the result. The sols are coagulated by CO₂ owing to the conversion of AgOH into Ag₂CO₃ and the consequent destruction of the source of AgO'. Electrolytes that do not form insol. Ag compounds behave normally, whilst those that do form such compounds bring about changes which vary with the relative amounts of Ag and electrolyte. KI reacts with the AgOH (or AgO') to give AgI and, if present in excess, AgI₂'. Hence with a deficit of KI the stabilising AgO' is removed and coagulation ensues, whilst with excess of KI a second stabilising ion AgI₂' is formed and eventually the whole of the Ag is converted into a sol of AgI stabilised by AgI₂'. These changes occur only in the presence of O₂, which oxidises the exposed surface of the Ag and thus enables the above reaction to proceed to completion. Na₂S₂O₃ also reacts with AgO' to give a complex Ag ion capable of stabilising the sol. Sols stabilised with Na₂S₂O₃, also those that have been long in contact with glass and are then stabilised by a silicate ion, are no longer coagulated by CO₂. F. L. U.

Burton's rule for positive hydrosols. I. General and preparative. H. Kauffmann (*Kolloid-Z.*, 1940, 92, 343—354).—An improved arrangement is described for the electrical dispersion of Fe, Al, and Cu (as oxides) in H₂O, consisting essentially in attaching one electrode to the armature of an a.c. electromagnet operating on a 50-cycle supply. The relative movement of the electrodes thus produced effectively prevents their welding together and trebles the max. concn. of colloidal material attainable (e.g., 1.24 g. Cu per l. instead of 0.4 g.). Sols of CuO, Al₂O₃, and Fe₂O₃ have been prepared in this manner, the last two also by hydrolysis of the chlorides, and purified by dialysis for the experimental study of the applicability of Burton's rule, with regard to which the available data are inconclusive. F. L. U.

Effect of strong electrolytes on the viscosity of quartz suspensions. A. von Buzagh and E. Erenyi (*Kolloid-Z.*, 1940, 91, 279—287).— η_{rel} for pure quartz suspensions is given by $\eta_{rel} = 1 + k_1c + k_2c^2$; is almost independent of particle radius (r) but k_2 decreases with increasing r . In 0.1M-BaCl₂ $\eta_{rel} = 1 + kc$ but k is $>$ the val. required by the Einstein relation, and decreases with increasing r . The effect is due to dehydration and charge neutralisation by BaCl₂, thus increasing the particle cohesion. It is found that k varies with r in the same way as the cohesion determined in other ways. Other salts also increase η_{rel} and their relative effects follow the valency and lyotropic series rules. AlCl₃ and Th(NO₃)₄ show a max. in the curves, and for acids these curves are steeper than for neutral salts. NaOH has little effect on η_{rel} . The univalent ions (but not the bivalent) agree with the theory of Ostwald connecting η_{rel} and activity. J. H. BA.

Ionic exchange on colloidal sulphur. II. Ionic exchange on lyophobic colloidal systems. E. O. K. Verstraete (*Kolloid-Z.*, 1943, 103, 25—42).—Displacement of H⁺ ions on S sols by other cations was measured by determining the acid-equiv. of the sol and of the ultra-filtrate before and after addition of electrolyte. The extent

of exchange by different ions is in the order Ba $>$ Sr $>$ Ca $>$ K $>$ Na $>$ Li $>$ Mg. With cations of valency >2 coagulation of the sol is so rapid that complete exchange does not occur, and other disturbing factors operate. The radius, polarisability, and degree of hydration of ions are considered to be the factors determining extent of displacement. The antagonism between H⁺ or Na⁺ and other cations is studied. It can be partly but not wholly accounted for if ionic concns. are replaced by activities. R. H. F.

Sedimentation volume and anomalous flow in lyophobic suspensions. W. Gallay and I. E. Puddington (*Canad. J. Res.*, 1943, 21, B, 171—178).—The sedimentation vol. (v) of dried starch, MgO, Fe₂O₃, and talc in dry org. solvents is almost independent of the solvent, but with addition of H₂O v increases. In the case of talc and Fe₂O₃ addition of large amounts of H₂O to non-polar solvents brings about a reduction in v to a val. approaching that in pure H₂O. The increase in v is relatively large for anisodimensional particles like talc and small for spherical particles like starch. The increase in v is related to the degree of flocculation in the system, leading to a rigid branched-chain scaffolding type of structure. C. R. H.

Hydration of starch below the gelatinisation temperature. W. Gallay and I. E. Puddington (*Canad. J. Res.*, 1943, 21, B, 179—185).—The sedimentation vol. (v) of aq. starch suspensions below the gelatinisation temp. and the ease of redispersion of the sediment increase with temp. At the lowest temp. investigated (3°) the suspensions show considerable dilatancy; at 50° some flocculation occurs. Between these temp. hydration increases continuously with temp. Starch dried at 45° in a vac. shows no dilatancy when dispersed with H₂O, indicating that drying has affected its hydration capacity. Drying increases v and lowers the gelatinisation temp.; normal v , dilatancy, and gelatinisation temp. are restored if the dried starch is allowed to regain its moisture. The heat of wetting of dried starch is considerable and may result in local gelatinisation at the surface of the granules, leading to sticking and increased v . C. R. H.

Swelling and solubility of macromolecular materials. J. N. Brønsted (5 *Nordiske Kemikermøde*, 1939, 188).—The swelling of macromol. materials in contact with liquids is to be considered as dissolution where the potential energy is kinetic energy of the solute mols. Consequences are discussed. M. H. M. A.

Structural mechanics of visco-elastic continua. VII. Viscosity and chemical constitution of macromolecular systems. H. Umstätter (*Kolloid-Z.*, 1943, 103, 7—18).—Theoretical. A η -concn. function incorporating Staudinger's relation is derived thermodynamically, and the limits of its validity are examined. Macromols. are non-rigid and can therefore absorb part of the energy of solvent mols. on collision. Such inelastic collisions result in the formation of a sheath of solvent mols. around the solute mol.; solvation is thus accounted for without assumption of any special forces. Determination of particle size is possible from the flow curve and η -temp. function. Large mols. may rupture if the mol. cohesion between neighbouring chains is $>$ the chain strength. There is thus an upper limit to mol. size above which mols. are mechanically unstable. R. H. F.

Constitution of soap solutions. P. Ekwall (5 *Nordiske Kemikermøde*, 1939, 254).—A discussion of the properties of dil. soap solutions between the "crit." and "limiting" concns. At concns. $<$ the latter soap behaves as a normal uni-univalent electrolyte. M. H. M. A.

Measurements on the dialysis of aqueous soap solutions. O. Lamm (*Kolloid-Z.*, 1940, 91, 275—279).—The rates of dialysis of KOAc and Na laurate (I) are compared when dialysis occurs into a small vol. of H₂O to prevent hydrolysis. The rate for KOAc can be accounted for theoretically and that for (I) follows the same equation until the concn. in the small vol. is ~ 0.022 , after which the rate is $<$ the theoretical. This is not due to loss of permeability of the membrane or to membrane hydrolysis, but probably arises from micelle formation. The decrease in rate occurs at about the same concn. as a decrease in the free diffusion of (I). J. H. BA.

Relations between electrical conductivity and degree of dispersion of lyophilic colloids. III. Conductivity of sodium and potassium palmitate and stearate solutions in presence of *m*- and *p*-cresol. E. Angelescu and A. Woinarosky (*Kolloid-Z.*, 1940, 92, 355—361).—The conductivity of Na and K palmitates and stearates has been determined over the range 20—60° in 0.1 and 0.2N. solution in the presence of varying amounts of *m*- and *p*-cresol. The influence of the length of the hydrocarbon chain, of the soap cation, and of the concn. of the cresol is the same as for *o*-cresol (cf. A., 1943, I, 305). A comparison of the influence of the cresols on η (large effect) and on conductivity (small effect) indicates that the particles giving rise to increased η are not identical with those responsible for conduction. F. L. U.

Kinetic theory of rubber. F. C. Auluck and D. S. Kothari (*J. Chem. Physics*, 1943, 11, 387—392).—Mathematical. Young's modulus for ideal rubber has been calc. by a statistical method, defining the macro-state of a chain-mol. by its length and not by the distance between the ends. W. R. A.

Elasticity of a network of long-chain molecules. II. L. R. G. Treloar (*Trans. Faraday Soc.*, 1943, 39, 241—246; cf. A., 1943, I, 90).—Wall's treatment of the elasticity of a mol. network is extended to the general homogeneous type of deformation of rubber. An equation is derived for the work of deformation in terms of the three principal strains, from which some general stress-strain relations, involving only one physical const. of the material, are deduced. The formulæ are applied to some simple cases.

F. L. U.

Fast and slow extension of plastic materials. R. N. Haward (*Trans. Faraday Soc.*, 1943, 39, 267—280).—The work absorbed by a material under impact is considered to be governed either by the rate at which deformation can occur or by the amount of deformation possible. Results of experiments on the extension, at different rates, of celluloid, cellulose acetate, and poly-Me methacrylate are discussed, and it is concluded that the concept of "ideal total work," viz., the sum of the Hookean and non-ideal elastic work, each taking place at the max. initial stress, can be used in conjunction with that of the crit. impact velocity to bring fast and slow deformations of plastic material into a single picture. Experiments on the extension and breaking of cellulose acetate at different temp. indicate that adiabatic temp. changes during extension will not be large enough to alter the character of the deformation.

F. L. U.

Gel formation in vinyl-divinyl copolymers. W. H. Stockmayer and H. Jacobson (*J. Chem. Physics*, 1943, 11, 393).—The gel-point in the copolymerisation of vinyl and divinyl reactants permits the determination of the wt. average no. of reacted double bonds in a stable polymer chain.

W. R. A.

Rheometry of organic glasses. I. W. Scheele, M. Alfeis, and L. Lahaye (*Kolloid-Z.*, 1943, 103, 1—7).—Org. glasses are classified according to the type of flow curve obtained on subjecting them to deforming stresses. For pure flow the material is characterised by its η ; for quasi-flow η varies with applied stress. Measurements are made of velocity of flow of 4 polyvinyl acetates of varying degrees of polymerisation at temp. from 35° to 110° using Hoppler's consistometer. For evaluation of the flow curves the concept of work of deformation is developed and shown to be a useful criterion of the material. Its log bears a linear relation to the reciprocal of the abs. temp. for the materials and temp. range examined.

R. H. F.

Structures of cellulose fibres. H. Ruska (*Kolloid-Z.*, 1940, 92, 276—285).—Electron-micrographs of transverse sections of cotton hairs and artificial cellulose fibres show a compact outer wall enclosing a matrix permeated by hollow spaces.

F. L. U.

Biocolloids as high-molecular electrolytes. III. (a) Sphingomyelin. (b) Position of rubidium and caesium in the series of active alkali cations. H. G. Bungenberg de Jong, L. Teunissen-van Zijp, and P. H. Teunissen (*Kolloid-Z.*, 1940, 91, 311—315).—A pure specimen of sphingomyelin has been prepared, the charge reversal concn. for UO_2^{2+} , Ce^{4+} , La^{3+} , $\text{Co}(\text{NH}_3)_6^{3+}$, Pb^{2+} , Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , Li^+ , Na^+ , and K^+ obtained, and the reciprocal hexol no. determined. The vals. agree with those of other phosphate colloids (A., 1938, I, 467). In general the charge reversal concn. is lower (except for Na^+ and K^+) for specimens with higher reciprocal hexol no., i.e., higher purity. The charge reversal concns. of Rb and Cs for Na agar, Na pectinate, ovolécithin, and soya-bean phosphatide are determined and placed in the alkali cation series previously obtained. They agree with the proposed theory concerning the polarisability of the ionogenic group and that of H_2O .

J. H. BA.

Electrophoretic behaviour of hydrocarbons and the influence of temperature thereon. H. W. Douglas (*Trans. Faraday Soc.*, 1943, 39, 305—311).—Mobilities of particles of dodecane (I), paraffin wax (II), and Δ^8 -octadecene (III) in aq. dispersions 0.01N. in Na^+ have been measured at pH 2—12. The ζ -pH curves for (I) and (II) are nearly coincident, whilst that for (III) rises more steeply. Mobilities increase with rise of temp. at a given pH, but the ζ -potential is substantially unaffected over the range 25—40°. The heat of adsorption of OH^- is calc. to be ~ 800 g.-cal. per g.-ion of OH^- adsorbed.

F. L. U.

initial concn. In the action of 40.8% aq. HCl on cellulose, complete hydrolysis to (I) occurs, and the reversion equilibrium is reached in 25 hr. at 20°.

F. L. U.

Dissociation of hexa-arylethanes. Equilibria involving "mixed ethanes." C. M. Himel and M. B. Mueller (*J. Amer. Chem. Soc.*, 1943, 65, 1654—1656).— K_{12} for $\text{E}_{12} \rightleftharpoons \text{R}_1 + \text{R}_2$, where R_1 , R_2 are different triarylmethyls and E_{12} is the corresponding hexa-arylethane, have been calc. from the data of Marvel and Himel (A., 1943, II, 27). Mixed ethanes have ΔG of dissociation $>$ that of the parent compounds, since $K_{12} < K_1 (\text{E}_{11} \rightleftharpoons 2\text{R}_1)$ and $K_2 (\text{E}_{22} \rightleftharpoons 2\text{R}_2)$. K_{12} may depend not only on K_1 and K_2 but also on the polarisation of the ethane linking, steric hindrance, or the effect of symmetry on ΔS of dissociation.

W. R. A.

Additive compounds of sulphur dioxide. N. F. Albertson and W. C. Fernelius (*J. Amer. Chem. Soc.*, 1943, 65, 1687—1690).—The binary systems SO_2 and dioxan, PhOMe , Et_2S , COMe_2 , NHPhMe , $(\text{CH}_2)_2\text{O}$ are discussed. New compounds (1:1) between SO_2 and dioxan, $(\text{CH}_2)_2\text{O}$, PhOMe , and Et_2S and a (1:2) SO_2 -dioxan compound are reported.

W. R. A.

Behaviour of trimethylamine, trimethylamino-sulphur trioxide, and trimethylamine oxide towards sulphur dioxide. A. B. Burg (*J. Amer. Chem. Soc.*, 1943, 65, 1629—1635).— NMe_3 with SO_2 gives NMe_3SO_2 for the dissociation of which ΔG° is 28.95 — 0.07404T kg.-cal. Extensive solvation occurs in liquid SO_2 but no definite secondary additive compounds, no ionisation, and no association were observed. Anhyd. NMe_3O absorbs SO_2 at -80° and yields $\text{NMe}_3\text{O}_2\text{SO}_2$ which readily loses SO_2 to give the very stable $\text{NMe}_3\text{O}_2\text{SO}_2$. This compound appears to be dimeric in solution in SO_2 . The type of linking is discussed from the electronic point of view.

W. R. A.

Constitution of ammoniacal solutions of mercuric salts. J. Bjerrum (5 *Nordiske Kemikermøde*, 1939, 195—196).—Acid and alkaline $\text{Hg}(\text{NO}_3)_2$ -0.5—2.0N- NH_4NO_3 solutions contain only amino- and no hydroxo-complexes. Vals. for $\log K_n$ ($K_n = [\text{Hg}(\text{NH}_3)_n]^{2+}/[\text{Hg}(\text{NH}_3)_{n-1}^{2+}][\text{NH}_3]$) at room temp. are: $n = 1, \sim 8.8$; 2, ~ 8.7 ; 3, 0.83; 4, 0.95.

M. H. M. A.

Refractometric investigations on three systems of aluminium nitrate and sodium acetate, tartrate, and citrate. G. Spacu and E. Popper (*Kolloid-Z.*, 1943, 103, 19—24).—Refractive indices (n) of aq. solutions of $\text{Al}(\text{NO}_3)_3$ and NaOAc , Na tartrate and citrate and of binary mixtures of these are recorded. For mixtures the deviation between n observed and n calc. from the vals. for the components exhibits a max. at a certain concn. ratio in each case. This is attributed to complex formation, the compositions of the max. corresponding to the following complexes: $[\text{Al}_2(\text{OAc})_4(\text{OH})_2]\text{OAc}$, $[\text{Al}_2(\text{C}_4\text{H}_4\text{O}_7)_2(\text{OH})_2]\text{Na}_2$, and $[\text{Al}_2(\text{C}_6\text{H}_5\text{O}_7)_2]\text{Na}_2$ or $[\text{Al}_2(\text{C}_6\text{H}_5\text{O}_7)_2(\text{OH})_2]\text{Na}_2$. The failure of OH^- ions to ppt. Al in presence of acetates, tartrates, and citrates is accounted for by the formation of these complexes.

R. H. F.

Solubility and dissociation of cryolite in aqueous solutions.—See A., 1944, I, 12.

Rates and equilibria in the ionisation of C—H bonds. R. P. Bell (*Trans. Faraday Soc.*, 1943, 39, 253—259).—Data for the rates of ionisation of 12 carbonyl compounds in presence of bases and for the dependence of the rate on basic strength are used to deduce approx. vals. of the acid dissociation const. K_A . This ranges from 10^{-8} for $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ to 10^{-20} for COMe_2 . K_A calc. for COPhMe is 10^{-18} , and for CH_2Ac_2 is 10^{-9} , both in agreement with other experimental data; the val., 1.5×10^{-6} , usually quoted for CH_2Ac_2 is incorrect. Reasons are given for considering the activity of unassociated H_2O in water at 25° to be $\sim 0.13M$, and if this val. is used to estimate the basic strength of OH^- the rates of ionisation of ketones in presence of OH^- show approx. agreement with other kinetic and equilibrium data, though there are some unexplained discrepancies. In the reaction $\text{RH} + \text{B} \rightleftharpoons \text{BH} + \text{R}^-$ (RH = carbonyl compound, B^- = base) the effect of substituents in either reactant is to shift the potential energy curves along the energy axis without seriously changing their shape.

F. L. U.

Basic strength of organic oxides of the elements of the nitrogen and sulphur groups. P. Nylen (5 *Nordiske Kemikermøde*, 1939, 227—229).— pK_A has been determined at 20° for $\text{R}_2\text{X}\cdot\text{O}$ and R_2ZO ($\text{R} = \text{Me}, \text{Et}$; $\text{R}' = \text{Me}, \text{Et}, \text{Ph}$, o - and p - C_6H_4 ; $\text{X} = \text{N}, \text{P}, \text{As}, \text{Sb}$; $\text{Z} = \text{S}, \text{Se}, \text{Te}$). (Cf. A., 1942, I, 266.)

M. H. M. A.

Simple approximate relation between successive dissociation constants of symmetrical inorganic oxygen acids. T. L. Hill (*J. Amer. Chem. Soc.*, 1943, 65, 1564—1566).—An equation is derived, with which, provided that two K are known, further K of symmetrical inorg. O acids may be calc. The equation has been tested for neutral and charged oxyacids of P, As, S, Se, Te, and I. The equation is not restricted as to solvent.

W. R. A.

Effect of sodium chloride on the ionisation of boric acid at various temperatures. B. B. Owen and E. J. King (*J. Amer. Chem. Soc.*,

VI.—KINETIC THEORY. THERMODYNAMICS.

Reactions in the system cellulose-hydrogen chloride-water. III. Reversion of glucose and degradation of cellulose by concentrated hydrochloric acid. H. Frahm (*Ber.*, 1941, 74, [B], 622—635; cf. B., 1943, II, 314).—The condensation of glucose (I) dissolved in 40.8% aq. HCl is a strictly reversible reaction conforming with the law of mass action. Equilibrium consts. determined for a series of concns. of (I) indicate that the main reactions are $2(\text{I}) \rightleftharpoons \text{birose} + \text{H}_2\text{O}$, $(\text{I}) + \text{birose} \rightleftharpoons \text{triglucosan} + 2\text{H}_2\text{O}$, and $2 \text{birose} \rightleftharpoons \text{tetraglucosan} + 2\text{H}_2\text{O}$. The anhydrides are non-reducing. Variations of the equilibria with temp. are slight, and lead to a val. ~ 2 kg.-cal. per mol. for the heat of reaction. The % of reversion products in the equilibrium mixture increases with the initial concn. of (I), but the highest yield of birose relative to anhydrides is obtained with a low

1943, 65, 1612—1620).—A method of determining the ionisation of a weak acid in salt solutions by means of cells containing buffered solutions without liquid junctions is described, which by changing the standard state to conform with each salt concn. is equiv. to the method of determining K in pure H_2O . E° of the new standard states are given over a wide range of salt concn. and temp. K° of HBO_2 at seven concns. of $NaCl$ between 0.02 and 3.0M. and at 5° intervals between 5° and 55°, have been determined. Calc. vals. for $[\gamma_{H_2BO_2}/\gamma_{HBO_2}]_{M}$, ΔH° , ΔC° , and ΔS° at various temp. are given. W. R. A.

Acidic dissociation constants of phenoxyacetic acid and its derivatives. N. V. Hayes and G. E. K. Branch (*J. Amer. Chem. Soc.*, 1943, 65, 1555—1564).—Vals. of K at 25° for aq. $OPh\cdot CH_2\cdot CO_2H$ (I) and 26 of its derivatives have been determined, and compared with those of $BzOH$ and its derivatives. Excepting bromo- and iodo-phenoxyacetic acids, which are anomalously weak, K of m -derivatives can be calc. from those of the corresponding benzoic acids by Hammett's equations (cf. A., 1937, I, 142), whereas with p -derivatives, in which the substituent resonates strongly with the nucleus, calc. vals. are < the experimental vals. In o -derivatives the calc. vals. are > the experimental. An explanation, based on the differences between resonance in derivatives of (I) and $BzOH$, is advanced. W. R. A.

Constants in the Debye-Hückel equation for activity coefficients. G. G. Manov, R. G. Bates, W. J. Hamer, and S. F. Acree (*J. Amer. Chem. Soc.*, 1943, 65, 1765—1767).—The fundamental consts. given by Birge (*Rev. Mod. Physics*, 1941, 13, 233) and Wensel (A., 1939, I, 420) have been used to calc. the vals. of the consts. A and B (for unit vol. of solution and for unit wt. of solvent) of the Debye-Hückel equation for activity coeffs., and of $2.30259RT/F$ at temp. from 0° to 100°. Contributions of ϵ of the medium and of resonance between ions to the higher terms of the Debye-Hückel equations are discussed. W. R. A.

Theory of new phase formation: cavitation. J. B. Zeldovitch (*Acta Physicochim. U.R.S.S.*, 1943, 18, 1—22).—The probability of formation of a bubble in a liquid is treated as a particular case of the formation of a new phase. An equation of the Fourier-Fick type is obtained for the relationship between the rate of the direct and reverse processes of nucleus formation. In the case of cavitation, with a fluid of low v.p. under the action of a high negative pressure, the rate of formation of nuclei is determined by the η of the fluid. The dependence of the probability of cavitation on the duration of application of the negative pressure, and on the vol. of the region submitted to that pressure, is investigated. A. J. M.

Range of existence of liquid crystals in the system potassium [salt of] methyl-orange-water. F. Branner (5 *Nordiske Kemikermøde*, 1939, 207—209).—The system Me-orange K salt (I)— H_2O has been studied at atm. pressure at room temp. to >80°. (I), $2H_2O$ (rhombic) (stable at room temp. in presence of saturated solution) is converted, in presence of H_2O , at 36° into a two-phase mesomeric system, whence a buttery form of (I) (probably + $1H_2O$) can be separated by filtration. The buttery form decomposes at 80° into anhyd. (I) + saturated solution. The clearing curve of the mesomeric system has been studied from 36° to 80° (0.1M. clears at 55°); hysteresis is exhibited. M. H. M. A.

Nature of the difference in the constitution diagram of higher fatty acids and triglycerides. G. B. Ravitsch and V. A. Volnova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 37, 59—62).—The constitution diagrams of stearic and palmitic acids and of the corresponding triglyceride system tristearin-tripalmitin are compared and explanations of differences are discussed. N. M. B.

Equilibrium between silver bromide-chloride mixed crystals and bromide-chloride ions in solution. H. Flood (5 *Nordiske Kemikermøde*, 1939, 191—192).—The results of Eastman and Milner (A., 1934, 31) have been confirmed over the whole range of $AgCl$ - $AgBr$ solid solutions, which are thus regular solutions. $\Delta H \propto N_{AgCl}N_{AgBr}$, explaining the variation of K with composition of the solid phase. M. H. M. A.

Heats of formation of MgO , $MgCl_2$, $MgCl_2\cdot H_2O$, $MgCl_2\cdot 2H_2O$, $MgCl_2\cdot 4H_2O$, and $MgCl_2\cdot 6H_2O$. C. H. Shomate and E. H. Huffman (*J. Amer. Chem. Soc.*, 1943, 65, 1625—1629).—By measuring the heats of dissolution of these substances and Mg metal in 1.0N-HCl the following vals. for heats of formation ($\Delta H_{298.15}$) have been obtained: MgO —143,840, $MgCl_2$ —153,220, $MgCl_2\cdot H_2O$ —230,970, $MgCl_2\cdot 2H_2O$ —305,810, $MgCl_2\cdot 4H_2O$ —453,820, $MgCl_2\cdot 6H_2O$ —597,240 g.-cal. per mol. W. R. A.

VII.—ELECTROCHEMISTRY.

Electrical conductivity of sodium deuteroxide in heavy water. *Nordiske Kemikermøde*, 1939, 188—189).—Determined carried out at 18° and 25°. M. H. M. A.

Electrical conductivities of salts and solubilities of barium sulphate in water-ethyl alcohol solutions. B. Norberg and C. J. Clemmedson (*Arkiv Kemi, Min., Geol.*, 1943, 16, A, No. 4, 9 pp.).—Vals. of Λ at 25° have been determined for solutions of KI , KCl , K_2SO_4 , and $BaCl_2$ in 10 and 20 wt.-% aq. $EtOH$, and of KI , KCl , $LiCl$, Li_2SO_4 , and $BaCl_2$ in 30 and 40 wt.-% $EtOH$. Vals. of Λ_0 and the ionic mobilities are calc. and discussed with reference to Walden's rule and the Onsager theory. Vals. of the solubility of $BaSO_4$, deduced from Λ measurements, range from 3.270×10^{-5} (H_2O) to 4.771×10^{-7} g.-equiv. per l. (40 wt.-% $EtOH$). A. J. E. W.

Electrical conductivity of colloids.—See A., 1944, I, 13.

Differential moving boundary method for transference numbers. L. G. Longworth (*J. Amer. Chem. Soc.*, 1943, 65, 1755—1765).—The movement of the boundary between regions of different concn. of the same electrolyte has been studied by the schlieren scanning method. Displacements $\propto \partial n/\partial c$ (n = transference no.), and the behaviour of $\partial n/\partial c$ in the concn. range of the boundary may be deduced from the schlieren patterns. The method compares favourably with the direct moving boundary method, and is applicable to salt solutions at concns. for which the latter method cannot be used. A solution, in good agreement with experimental data, of the differential equation for concn. boundaries is given for the case in which one boundary moves as a steady state. W. R. A.

Transport numbers of aqueous silver nitrate in the presence of sucrose and measurements of the conductivity, viscosity, density, and refractivity. D. N. Solanki and S. Mukerji (*J. Indian Chem. Soc.*, 1943, 20, 93—96).—The transport nos. of the ions in $m/18$ - $AgNO_3$ in the presence of 0—150 g. of sucrose (I) per l. have been measured at 25°. Conductivity, η , d , and n_D data are also recorded. The transport no. of the Ag ion decreases with increasing (I) concn., reaching a min. with ~100 g. of (I) per l. and then increasing rapidly, whereas the η is a min. with ~25 g. of (I) per l. and the other properties change linearly with the (I) concn. The results are attributed to the hydration of the (I) mols. J. W. S.

Formal electrode potentials of palladium in aqueous hydrochloric and perchloric acid solutions. Stability of chloropalladate ion. D. H. Templeton, G. W. Watt, and C. S. Garner (*J. Amer. Chem. Soc.*, 1943, 65, 1608—1612).—The formal electrode potential, E° , of Pd^{II} salts in 0.9952N-HCl has been determined at 15°, 25°, and 35°, and is const. over a 50-fold range in concn. of Pd^{II} salt. E° at 25° has been measured in HCl - $HClO_4$ mixtures, such that total acid concn. and ionic strength were const., and in 4N- $HClO_4$. Pd^{II} exists in Cl^- solutions mainly as $PdCl_4^{2-}$. The potential for the half-cell reaction $Pd(s) + 4Cl^- (1f) = PdCl_4^{2-} (1-4fHCl) + 2e$ is $-0.6290 + 0.0080 \mu v.$ [$1.0 < \mu < 4.0$]; temp. coeff. 0.00046 v. per degree. Related thermodynamic consts. have been computed. For the half-cell reaction $Pd(s) = Pd^{II} (4fHClO_4) + 2e$, E°_{25} is -0.987 v. The val. of K for the dissociation of $PdCl_4^{2-}$ at 25° is $\sim 6 \times 10^{-14}$. W. R. A.

Electrochemical behaviour of the lead-tin couple in carbonate solutions. G. Derge, H. Marcus, and A. H. Grobe (*Amer. Inst. Min. Met. Eng., Tech. Publ.* 1447, 1942; *Metals Tech.*, 9, No. 3, 7 pp.).—Measurements were made of (1) the potentials of Pb and Sn, and (2) currents produced when Sn and Pb electrodes were connected, in Na_2CO_3 - $NaHCO_3$ solutions, pH 8.4—11.2. At pH 8.4 Pb is anodic to Sn, but at pH 9.5 to 11.2 Pb is cathodic. At pH 11.2 additions of Ag^+ , Bi^{3+} , Cu^{2+} , and Zn^{2+} have little effect; Ni^{2+} and agar-agar reduce the current without altering the potential; K_2CrO_4 and Na silicate lower potential and current, and reverse polarity. R. Ke.

Discharge of hydrogen ions. I. Mercury. A. Frumkin (*Acta Physicochim. U.R.S.S.*, 1943, 18, 23—57).—The vol. of H_2 liberated on a Hg cathode was determined in 3N-HCl, 2.2N-HBr, and 3N-KI — 0.1N-HBr. The results confirm the dependence of overvoltage (η) on c.d. Tafel's equation, $\eta = a + b \log i$ (i = current, a and b = const.) holds for Hg up to a high c.d. Using a dropping Hg electrode, measurements of η at const. i should give a mean val. 0.008 v. > the val. at const. potential. Comparison of electrocapillary curves of acidified and alkaline solutions shows the absence of at. H on the surface of the Hg. The mean val. of η on Hg for 0.1N-HCl, 0.2N-HBr, and 0.1N- H_2SO_4 at 20° is 1.428 + 0.115 $\log i$. When salts of multivalent cations (La^{3+} and Th^{4+}) are added to dil. solutions of acids, the val. of the potential changes from — to +. The increase of η produced by the addition of these ions is < the increase in the ψ_1 potential. When salts with a common anion are added to HCl or HBr, a decrease of η is observed for low c.d., but an increase for high c.d., except when Na_2SO_4 is added to H_2SO_4 , when there is an increase of η for all c.d. A. J. M.

Hydrogen overvoltage, especially on cementite. E. Palmær (5 *Nordiske Kemikermøde*, 1939, 260—261).—The H η is 0.06 ± 0.009 v. for Fe, and 0.12 ± 0.03 v. for cementite (no temp. given). Vals. are determined at low c.d. (>0.8 μa . per cm^2) to prevent depletion of H^+ around the cathode; other precautions are described. M. H. M. A.

VIII.—REACTIONS.

Hydroxyl in flames. II. Hydroxyl in the acetylene flame. L. I. Avramenko (*Acta Physicochim. U.R.S.S.*, 1943, 18, 58—68).—There is a linear dependence of the concn. of non-excited and excited OH on the rate of combustion of a C₂H₂–air mixture. The stoichiometric mixture of air and C₂H₂ gives a max. [OH], and such a mixture has max. rate of combustion. The emission spectrum of OH in a rarefied C₂H₂–air flame has been investigated, and it is shown that the method may be used to determine [OH] and [OH]. A. J. M.

Interchange of hydrogen isotopes with complex salts. I. Kinetics of the interchange with the luteocobaltic complex. J. S. Anderson, H. V. A. Briscoe, and N. L. Spoor. **II. Kinetics of the interchange with platinum and palladium tetramines.** J. S. Anderson, H. V. A. Briscoe, L. H. Cobb, and N. L. Spoor (*J.C.S.*, 1943, 361—367, 367—372).—I. In contact with H₂O, D-containing [Co(NH₃)₄]Cl₂ (I) and [Co en₃]Cl₂ (II) [en = (CH₃)₂NH₂], undergo isotope exchange at a rate v which follows a pseudo-unimol. law. The reactions have activation energies 28,400 and 28,100 g.-cal. per g.-mol. with (I) and (II), respectively. In both cases $v \propto 1/[H^+]$, but is almost independent of the concn. of ammine or the proportion of D which it contains. It is suggested that the Co–NH₃ group can ionise as an acid, giving Co–NH₂⁺ and H⁺, thus resembling aquo-ammines which can yield hydroxo-ammines by dissociation.

II. From the rate of isotope exchange between D-containing [Pt(NH₃)₄]Cl₂ and [Pd(NH₃)₄]Cl₂ and H₂O it is inferred that the rate of interchange with different metal ammine ions follows the order of their stabilities, viz., Co > Pt > Pd. Besides interchange through dissociation yielding H⁺ ions, [Pd(NH₃)₄]Cl₂ also undergoes interchange in acid solution through reversible dissociation of NH₃ from the complex. The results are discussed in relation to the general theory of complex salts. J. W. S.

Kinetics and mechanism of the racemisation of optically active cobaltic trisdguanide complex. P. Ray and N. K. Dutt (*J. Indian Chem. Soc.*, 1943, 20, 81—92).—The rates of racemisation of *d*- and *l*-Co^{III} trisdguanidinium chloro-*d*-tartrate (I) and of *d*- and *l*-Co^{III} trisdguanidinium chloride (II) (A., 1942, II, 78) have been studied in aq. solution at 40–60°. The activation energies (g.-cal. per g.-mol.) and vals. of log PZ of the Arrhenius equation are *d*-(I), 21,350 and 9.14, *l*-(I) 22,310 and 9.8, (II) 13,930 and 4.16, respectively. Foreign cations retard the racemisation of active (II), Ca⁺⁺, Cu⁺⁺, Mn⁺⁺, and H⁺ having a most pronounced effect even at low concns., but the change is unaffected by anions other than OH⁻, which has a strong accelerating effect. The inversion is interpreted on the basis of an excited condition in which the mol. can assume a distorted form but with the bond angles between each pair unchanged at 90°. From this form the mol. can pass into either the *d*- or *l*-form on losing its excess energy. J. W. S.

Mechanism of the reaction between hydrogen sulphide and sulphur dioxide in liquid media. N. F. Albertson and J. P. McReynolds (*J. Amer. Chem. Soc.*, 1943, 65, 1690—1691).—The rates of reaction of H₂S and SO₂ in various liquids have been investigated. From these and previous data the following mechanism is proposed: (i) formation of a compound between H₂S and the medium by a H-bond, (ii) liberation of HS⁻ ions from the additive compound, (iii) reaction between SO₂ (or its additive compounds) and HS⁻ ions. W. R. A.

Blue perchromic acid. I. Kinetics of the decomposition of the blue perchromic acid in various organic media. S. Prakash and R. C. Rai (*Proc. Indian Acad. Sci.*, 1943, 18, A, 1—7).—Blue perchromic acid decomposes by a first-order reaction in org. solvents, with a distinct induction period. Vals. of k in Et₂O at 10°, 20°, and 30° are, respectively, 0.002125, 0.005273, and 0.01711—0.02241. Addition of 33% of C₆H₆, PhMe, and xylene increases k by factors 1.79, 2.57, and 3.28, respectively, at 30°. L. J. J.

Dilatometric method of measuring rates of reactions. Application to the rate of hydrolysis of acetal. L. K. J. Tong and A. R. Olson (*J. Amer. Chem. Soc.*, 1943, 65, 1704—1707).—The effects of ΔH of dissolution and reaction on the dilatometric determination of rate coeffs. have been analysed. ΔH of dissolution and hydrolysis of CHMe(OEt)₂ in H₂O, 4M-NaCl, and M-KNO₃, determined calorimetrically, are respectively: -4700, 4100; -4250, 5100; -5560, 4500 g.-cal. per mol. Vol. changes during hydrolysis in these systems have been investigated, using a magnetically stirred dilatometer, and the H⁺-catalysed rate coeff. at 25° is computed. W. R. A.

Absorption of oxygen by glutathione in alkaline solutions. II. Kinetics of the reaction at pH 13. M. B. Young and H. A. Young (*J. Amer. Chem. Soc.*, 1943, 65, 1681—1687).—The rate of absorption of O₂ by glutathione at pH 13.0—13.3, catalysed by Cu⁺⁺, has been measured at various pressures of O₂ and concns. of Cu⁺⁺ and glutathione. A rate law is given, and a mechanism proposed for the reaction. W. R. A.

Acid hydrolysis of *dl*-alkyl- β -*d*-glucosides. I. MacArthur (*Proc. Leeds Phil. Soc., Sci. Sect.*, 1943, 4, 69—74).—The hydrolysis of

dl- β -methylbutyl- (I) and of 10 *sec*-alkyl- β -*d*-glucosides by N-HCl at 80° follows a unimol. course, except towards the end of the hydrolysis when the hydrolysis coeff. (k) increases. k is practically independent of the length of the alkyl chain and of its stereochemical configuration, in contrast to hydrolysis with emulsin. k for (I) is approx. half of k for the *sec*-glucosides. C. R. H.

Kinetics of vinyl derivative polymerisation. J. Ahere, G. Goldfinger, H. Mark, and H. Naidus (*J. Chem. Physics*, 1943, 11, 379—386).—Equations for the initial over-all rate of reaction and for the no. average polymerisation degree are derived, assuming that activation occurs by collision of an unactivated monomeride with another mol., that ease of deactivation varies with the type of nucleus, that termination of growth occurs by collision with another growing chain, an activated monomeride, a catalyst mol., or with chain-breaking impurities, and that for a certain period a steady state of activated centres is maintained. Propagation by normal chain growth and by chain transfer is considered. The equations are compared with experimental data on styrene polymerisations. W. R. A.

Zone of activation in rate processes. R. M. Barrer (*Trans. Faraday Soc.*, 1943, 39, 237—241).—The physical and statistical basis of the zone theory of diffusion and viscosity is outlined. The criticism advanced by Eley (A., 1943, I, 203) is inapplicable to the author's work. Further experimental behaviour is described which is predicted by the zone theory but is contrary to the transition state theory. F. L. U.

Kinetics and mechanism of photographic development. D. A. Frank-Kamenetzki (*Acta Physicochim. U.R.S.S.*, 1943, 18, 91—92).—The exponential increase of velocity of linear growth of an individual Ag nucleus with time (Rabinovitch, A., 1943, I, 93) can be explained on the assumption that rate of development is determined by the electrochemical oxidation of the developer proceeding on the whole surface of the Ag nucleus, the deposition of Ag taking place, however, only on its perimeter. The theory of Anastasitsch (*ibid.*, 95) is discussed. A. J. M.

Catalysis of vanadate-hydriodic acid reaction by the oxalate ion. C. R. Viswanadham and G. Gopala Rao (*Current Sci.*, 1943, 12, 229).—Preliminary. C₂O₄²⁻ ions accelerate the vanadic acid–HI reaction. The catalysis is probably more concerned with the vanadate ion than with the HI, since the reactions Cr₂O₇²⁻–HI and Cr₂O₇²⁻–HBr are also accelerated by C₂O₄²⁻ but reactions of HI with oxidising agents dissimilar to vanadate are not affected. J. F. H.

Hydrolysis of hydrogen cyanide in acetic acid solutions with mineral acids as catalysts. V. K. Krieble, F. C. Duennebieber, and E. Colton (*J. Amer. Chem. Soc.*, 1943, 65, 1479—1482).—Hydrolysis of HCN, with HCl or H₂SO₄ as catalyst, has been investigated in aq. and glacial AcOH and in AcOH–Ac₂O mixtures. Rates of hydrolysis increase rapidly with decreasing [H₂O] in the solvent. HCl is the better catalyst, the rate being very sensitive to [HCl]. For HCl, the rate \propto (mean ion activity)². No correlation of rate and physical properties was possible with H₂SO₄ solutions. W. R. A.

Oxidation processes. XV. Effect of reducing agents on the auto-oxidation of photographic developing agents. A. Weissberger, D. S. Thomas, jun., and J. E. Lu Valle (*J. Amer. Chem. Soc.*, 1943, 65, 1489—1495).—The effect of ascorbic (I) and dihydroxymaleic acids on the autooxidation of *o*- and *p*-C₆H₄(OH)₂, ψ -cunoquinol (II), *p*-NH₂-C₆H₄-OH, metol, amidol, and *p*-C₆H₄(NH₂)₂ has been investigated. The retardation observed in most cases is explained by assuming that the quinonoid and semiquinonoid oxidation products catalyse the autooxidation, but are reduced by the inhibitors. (I) accelerates the autooxidation of (II) by the formation of semiquinones, which also explain the acceleration of the autooxidation of (I) by ψ -cunoquinone. W. R. A.

Activation of oxygen by solid surfaces.—See A., 1944, III, 63.

Mechanism of the steam-carbon reaction. B. R. Warner (*J. Amer. Chem. Soc.*, 1943, 65, 1447—1451).—Present data show that CO and H₂ are the primary products of the H₂O–C reaction and that CO₂ is formed by the reaction CO + H₂O \rightleftharpoons CO₂ + H₂ (I). The rate of gasification of C depends on the H₂ adsorption isotherm, becoming const. above a steam saturation pressure. CH₃O and HCO₂H are suggested as adsorbed intermediates in the reactions C + HO \rightleftharpoons CO + H₂ and (I), respectively. A theory for the catalysis of the steam–C reaction is proposed. W. R. A.

Catalytic hydrogenation of carbon monoxide. Methane synthesis from water-gas.—See B., 1943, II, 365.

Catalysts for synthesis of carbon disulphide.—See B., 1943, II, 365.

Electrolytic polishing of metals.—See B., 1943, I, 500.

The Schuster band of ammonia and electrical synthesis of hydrazine. E. J. B. Willey (*Trans. Faraday Soc.*, 1943, 39, 234—237).—Experiments on the decomp. of NH₃ in electrical discharges support the view (cf. A., 1933, 1232) that the Schuster band at λ 5635 originates in a reaction NH₃ + NH \rightarrow N₂H₄⁺ \rightarrow N₂H₄ + $h\nu$. F. L. U.

Photographic latent image. I. Lattice energy and related quantities for hypothetical silver bromide crystal having the cubic ZnS type of structure. II. Outline of theory. M. L. Huggins (*J. Chem. Physics*, 1943, 11, 412–419, 419–426).—I. Lattice energy, equilibrium distance between atoms, density, and energy changes associated with electronic and ionic shifts are calc. for the cubic NaCl (B_1) and cubic ZnS (B_3) structures of AgBr. The latter has slightly higher energy, but may be stabilised by an extra electron or Ag^+ ion. The B_3 structure has the higher ionic conductivity.

II. According to the theory suggested, the latent image consists of small regions of B_3 lattice structure in the Ag halide grains, stabilised by the presence of photo-electrons. The presence of an extra electron in a positive potential hole stabilises the B_3 structure by 0.6 e.v. Replacement of some Br by S, or of Ag^+ by Hg^{++} , or adsorption of polar dyes, should favour B_1 – B_3 transition by facilitating the capture of photoelectrons. L. J. J.

An effect in pure silver chloride crystals similar to the photographic Schwarzschild effect. P. Meiklar (*Compt. rend. Acad. Sci. U.R.S.S.* 1941, 31, 226–229).—The absorption curves for the Ag–AgCl system are calc. for different sizes of colloidal Ag particle from the Rayleigh and Mie equations, and these curves are used, in conjunction with the experimentally obtained absorption curves of exposed pure AgCl crystals, to determine the average size of the colloidal Ag formed under varying conditions of exposure. Using three different intensity levels and a no. of exposure times for each intensity level, it is found that at all intensity levels the colloidal Ag particle increases in size with increased time of exposure, but for a given exposure time the particle size is the smaller the higher is the intensity. Although the intensity level and exposure times are some thousand times those normally employed with photographic material, it is suggested that this effect of intensity on the dispersion of the Ag particle is a factor in the mechanism of the Schwarzschild effect. Contrary to the Gurney–Mott theory of latent image formation, it is considered that the liberated electrons do not wander from their point of liberation, but cause local concns. which result, at high intensities, in a more highly dispersed latent image Ag centre. J. W. G.

Activated oxalic acid. P. S. MacMahon and B. B. Lal (*J. Indian Chem. Soc.*, 1943, 20, 143–152; cf. A., 1941, I, 18).—No evidence was obtained for the existence of activated $\text{H}_2\text{C}_2\text{O}_4$. When $\text{N-H}_2\text{C}_2\text{O}_4$ is treated in absence of O_2 and light with small quantities of KMnO_4 or hydrated MnO_2 , there persists, for a few min. after the consumption of the latter, a brownish coloration, probably due to the unstable acid $\text{HMn}(\text{C}_2\text{O}_4)_2$. This is the active principle involved in the slow reduction of HgCl_2 . No reduction occurs if HgCl_2 is added after its disappearance. The statement of Oberhauser and Schormuller (A., 1929, 793) that KMnO_4 brings about this reduction in anhyd. COME, is not confirmed. In aq. solution, the replacement of KMnO_4 by Mn^{++} ions gave negative results. Excess of $\text{K}_2\text{C}_2\text{O}_4$ turns the brown solution pink with the formation of the more stable complex salt $\text{Mn}(\text{KC}_2\text{O}_4)_3$, which retains the ability to reduce HgCl_2 quantitatively for 24 hr. in the dark. This compound is produced when KMnO_4 in concn. $>10^{-5}\text{N}$. is slowly decolorised by $\text{N-K}_2\text{C}_2\text{O}_4$. In this case a non-linear relationship was observed between the quantity of KMnO_4 and the amount of reduction of HgCl_2 , which took several hr. to complete. With $0.1\text{N-K}_2\text{C}_2\text{O}_4$ the amount of reduction was about 10 times that obtained with $0.1\text{N-H}_2\text{C}_2\text{O}_4$ using the same quantities of KMnO_4 . The reduction mechanism is explained by a long-chain process initiated by the formation of active CO_2' (or $\text{C}_2\text{O}_4''$) ions $[\text{Mn}(\text{C}_2\text{O}_4)_2] \rightarrow \text{C}_2\text{O}_4'' + \text{Mn}(\text{C}_2\text{O}_4)_2$; $\text{Mn}(\text{C}_2\text{O}_4)_2 \rightarrow \text{Mn}(\text{C}_2\text{O}_4)_2 + \text{CO}_2 + \text{CO}_2'$. O_2 inhibits the reduction, although it actually lengthens the life of $\text{HMn}(\text{C}_2\text{O}_4)_2$, apparently by removing one of the chain-carriers. No evidence was obtained to support the postulation by Launer (A., 1933, 476) of the formation of CO_2' from CO_2 ions when applied to the $\text{I-C}_2\text{O}_4''$ reaction. This reaction is retarded by traces of Mn^{++} which is converted into $\text{Mn}(\text{KC}_2\text{O}_4)_3$ in diffused light. In air and in the dark Mn^{++} ions cause the reduction of HgCl_2 by $\text{K}_2\text{C}_2\text{O}_4$, after an induction period, with gradually increasing rate, $\text{Mn}(\text{KC}_2\text{O}_4)_3$ being formed simultaneously. No $\text{Mn}(\text{KC}_2\text{O}_4)_3$ was formed from Mn^{++} ions and $\text{K}_2\text{C}_2\text{O}_4$ alone until a trace of acid had been added. A mechanism not requiring the assumption of an activated form of $\text{H}_2\text{C}_2\text{O}_4$ is suggested for the atm. oxidation of $\text{H}_2\text{C}_2\text{O}_4$ with the formation of H_2O_2 catalysed by Mn^{++} ions. Hydrated MnO_2 reacts vigorously with conc. $\text{H}_2\text{C}_2\text{O}_4$ with CO_2 evolution, and a red filtrate can be obtained which will reduce HgCl_2 in air. It apparently contains a peroxalate or manganioxalic acid, $\text{Mn}(\text{HC}_2\text{O}_4)_3$, relatively stable in excess of conc. $\text{H}_2\text{C}_2\text{O}_4$. No other simple carboxylic acid will reduce HgCl_2 in presence of KMnO_4 . L. H. L.

Photochemical studies. XXXVI. Quantum yields during the photochemical decomposition of methyl *n*-butyl ketone. J. E. Wilson and W. A. Noyes, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 1547–1550).—Quantum yields of formation of the products of the decomp. of COMeBu^n have been determined as functions of I , p , λ , and T . Quantum yields of CO and C_2H_6 are small and increase with T , whereas those of the main products are independent of the variables

studied. No discrimination between a free radical mechanism and a primary decomp. into final products is possible. W. R. A.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Reactions of solid substances. CXXIV. Course of sintering in copper powder. G. F. Hüttig [with C. Bittner, R. Fehser, H. Hannawald, W. Heinz, W. Hennig, E. Herrmann, O. Hnevkovsky, and J. Pecher] (*Z. anorg. Chem.*, 1941, 247, 221–248).—Samples of pure, finely-divided Cu powder were heated in a stream of H_2 under const. conditions to temp. from 100° to 800° . After cooling, the photomicrograph, X-ray diagram, pyknometric d , vol. (shaken down), solubility in dil. HNO_3 , e.m.f., reactivity towards aq. AgNO_3 , MeOH adsorption isotherm, and the catalytic activity for the decomp. of H_2O_2 were measured. The method provides data only on the irreversible part of the process. At $\sim 400^\circ$ a considerable contraction occurs, which is preceded by a distinct expansion. A "preshrinking," coupled with a similar initial expansion, is observed at $\sim 200^\circ$. The change in the other properties measured, for the most part, parallel those of the vol. The two contractions differ in that at 200° the process is essentially confined to the surface whilst at 400° the whole lattice is involved. The expansions observed probably correspond with an activated intermediate state. J. F. H.

Complex cuprous thiosulphates. G. Spacu and J. G. Murgulescu (*Kolloid-Z.*, 1940, 91, 294–310).—Complexes $\text{XCu}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{X}_2\text{Cu}_2(\text{S}_2\text{O}_3)_2 \cdot x\text{H}_2\text{O}$ ($\text{X} = \text{NH}_4$, Na, K) are formed by addition of $\text{X}_2\text{S}_2\text{O}_3$ to $\text{Cu}(\text{NO}_3)_2$; their composition is checked by potentiometric titration and analysis of the ppts. In addition $(\text{NH}_4)_2\text{Cu}(\text{S}_2\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{K}_2\text{Cu}(\text{S}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$, and $\text{Na}_2\text{Cu}(\text{S}_2\text{O}_3)_2 \cdot x\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Cu}(\text{S}_2\text{O}_3)_2 \cdot 2\text{NH}_4\text{NO}_3$, $\text{K}_2\text{Cu}(\text{S}_2\text{O}_3)_2 \cdot 2\text{KNO}_3$, and $\text{Na}_2\text{Cu}(\text{S}_2\text{O}_3)_2 \cdot 2\text{NaNO}_3$ are formed. With $\text{Cu}(\text{ClO}_3)_2$ $(\text{NH}_4)_2\text{S}_2\text{O}_3$ gives $(\text{NH}_4)_2\text{Cu}(\text{S}_2\text{O}_3)_2 \cdot 2\text{NH}_4\text{ClO}_3$. J. H. B.A.

Behaviour of cadmium hydroxide and mercuric oxide towards alkalis. R. Scholder and E. Staufenbiel (*Z. anorg. Chem.*, 1941, 247, 259–276).—From solutions of $\text{Cd}(\text{OH})_2$ in conc. aq. alkalis the following cryst. *cadmates* were prepared: $\text{Na}_2[\text{Cd}(\text{OH})_4]$ (I), $\text{Na}_2[\text{Cd}(\text{OH})_4] \cdot \frac{1}{2}\text{NaOH} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ (II), $\text{Na}_2[\text{Cd}(\text{OH})_4] \cdot (\text{H}_2\text{O})_2$ (III), $\text{Sr}_2[\text{Cd}(\text{OH})_4]$ (IV), and $\text{Ba}_2[\text{Cd}(\text{OH})_4]$ (V). The hydroxy-salt nature of (I) is shown by the course of thermal dehydration of the compound. (II) and (III) lose the H_2O outside the complex over H_2SO_4 . At 100° the curve relating solubility of $\text{Cd}(\text{OH})_2$ to normality of NaOH is cusp-shaped with a break at 14.2N , owing to the solid phase becoming (I). From $\text{Cd}(\text{OH})_2$ –NaOH–NaBr solutions, $\text{Na}_2[\text{Cd}(\text{OH})_4] \cdot 7\frac{1}{2}\text{Br}_2 \cdot 2\text{H}_2\text{O}$ can be prepared. Conc. aq. KOH gives cryst. CdO and $\text{Cd}(\text{OH})_2$. No mercurates could be prepared, the product being cryst. HgO . From HgO –NaOH–Na halide solutions the compounds $2\text{HgO} \cdot \text{NaBr}$ and $2\text{HgO} \cdot \text{NaI}$ were obtained. J. F. H.

Addition of boron fluoride to hexamethylenetetramine. A. B. Burg and La V. L. Martin (*J. Amer. Chem. Soc.*, 1943, 65, 1635–1637).—By adding BF_3 to $(\text{CH}_2)_6\text{N}_4$ in liquid SO_2 the compound $(\text{CH}_2)_6\text{N}_4 \cdot 4\text{BF}_3$ is formed. At const. pressure BF_3 is removed without discontinuity as the temp. rises and tends towards a limit corresponding with $(\text{CH}_2)_6\text{N}_4 \cdot \text{BF}_3$. W. R. A.

Borohydrides of gallium. H. I. Schlesinger, H. C. Brown, and G. W. Schaeffer (*J. Amer. Chem. Soc.*, 1943, 65, 1786–1787).—When GaMe_3 is treated with excess of B_2H_6 at room temp. Ga and H_2 are identified among the products and the equation $\text{GaMe}_3 + 3\text{B}_2\text{H}_6 = \text{Ga} + 3\text{B}_2\text{Me}_3\text{H}_6 + 1.5\text{H}_2$ is suggested for the over-all reaction. This probably occurs by formation and autocatalytic decomp. of $\text{Ga}(\text{BH}_4)_3$ occurring thus: $2\text{GaMe}_3 + 9\text{B}_2\text{H}_6 = 2\text{Ga}(\text{BH}_4)_3 + 6\text{B}_2\text{Me}_3\text{H}_6 + 2\text{Ga}(\text{BH}_4)_3 = 2\text{Ga} + 3\text{B}_2\text{H}_6 + 3\text{H}_2$. At -45° dimethylgallium borohydride, GaMe_2BH_4 (I), is formed: $2\text{GaMe}_3 + 3\text{B}_2\text{H}_6 = 2\text{GaMe}_2\text{BH}_4 + 2\text{B}_2\text{Me}_3\text{H}_6$. The extrapolated b.p. of (I) is 92° and its Trouton's const. is 23.5. W. R. A.

Use of the exchange between carbon dioxide, carbonic acid, bicarbonate ion, and water for isotopic concentration. A. F. Reid and H. C. Urey (*J. Chem. Physics*, 1943, 11, 403–412).—The exchange of O and C in the reactions (i) CO_2 (dissolved) + H_2O \rightleftharpoons H_2CO_3 , (ii) CO_2 (dissolved) + $\text{OH}^- \rightleftharpoons \text{HCO}_3^-$ can be catalysed by solid surfaces, e.g., glass fibres, C , Al_2O_3 , increases in rate of up to 4 or 5 times and up to 2000 times, respectively, being found. Data for separation of O and C isotopes by a static bomb method and by fractionating columns at 1–50 atm. are recorded. L. J. J.

Silicon arsenides. W. Klemm and P. Pirscher (*Z. anorg. Chem.*, 1941, 247, 211–220).—Thermal analysis and X-ray investigation of the system Si–As reveal the existence of the compounds SiAs_2 , decomp. 944° , and SiAs , congruent m.p. 1083° . The compounds exist over a small range; Si and As dissolve in each other but slightly. Both compounds are formed with increase in vol. The properties of the compounds and the alloying properties of Si and Ge with the elements of groups IV and V are discussed. J. F. H.

Germanium (iso)cyanate. A. W. Laubengayer and L. Reggel (*J. Amer. Chem. Soc.*, 1943, 65, 1783–1784).—To GeCl_4 dissolved in

C_6H_6 was added powdered $AgOCN$ in small quantities through a reflux condenser. The mixture was heated on a H_2O -bath for 1 hr., allowed to cool, filtered, and the filtrate on fractional distillation gave $Ge(OCN)_4$, b.p. 195–199°. It is a colourless liquid (doubtful whether cyanate or isocyanate) with $\log_{10} p = 8.77-2764\theta$ ($\theta = 35^\circ$ to 140°), mol. heat of vaporisation 12.6 kg.-cal., m.p. -8° , $\rho_{25}^{25} 1.7694$, $n_D^{25} 1.4793$. W. R. A.

History of nitrogen tribromide. (A) L. Birckenbach and M. Linhard, (B) M. Schmeisser (*Z. anorg. Chem.*, 1941, **247**, 307, 308).—(A) A criticism of Schmeisser's claim to have first isolated a substance believed to be $NBr_3 \cdot 6NH_3$ (A., 1942, I, 274) which the authors had prepared previously (A., 1929, 1285).

(B) An apology.

J. F. H.

Behaviour of phosphoryl chloride, thionyl chloride, and sulphuryl chloride towards boron halides. A. B. Burg and M. K. Ross (*J. Amer. Chem. Soc.*, 1943, **65**, 1637–1638).—Neither $SOCl_2$ nor SO_2Cl_2 reacts with BF_3 or BCl_3 . Although $POCl_3$ does not react with BF_3 , it forms $POCl_3 \cdot BCl_3$, rhombic crystals having ΔG_{298}° of dissociation of ~ -4.6 kg.-cal.

W. R. A.

Polythionic acids and their formation. IV. Reactions between polythionic acids and sulphurous or thiosulphuric acid. H. Stamm, O. Seipold, and M. Goehring (*Z. anorg. Chem.*, 1941, **247**, 277–306).—Investigations were made of the systems polythionic acid– H_2SO_3 and polythionic acid– $H_2S_2O_3$ in aq. solution, in which the temp. ($10-40^\circ$), pH ($0-2$), and concn. of the reactants were altered. Tri- (I), tetra- (II), penta- (III), and hexa-thionic acid (IV) were used. (I) is not decomposed by H_2SO_3 at pH 1.6 except at 40° . (I) with $H_2S_2O_3$ reaches an equilibrium $H_2S_2O_3 + H_2S_2O_6 \rightleftharpoons H_2S_4O_6 + H_2SO_3$ (A), the equilibrium lying largely to the left at pH 1.6. The behaviour is complicated by the side-reaction: $H^+ + S_2O_6^{2-} \rightarrow HSO_3^+ + S$ (B). (III) is also formed. (II) mainly reacts with H_2SO_3 thus: $H_2S_4O_6 + H_2SO_3 \rightleftharpoons H_2S_5O_6 + H_2S_2O_6$ (C = A reversed) at pH 1.7. The reaction velocity (v) is increased by increase in $[H_2SO_3]$ but to a smaller extent by increase in $[H_2S_2O_6]$ since this also increases the velocity of the side-reaction: $H_2S_4O_6 + H_2S_2O_3 \rightleftharpoons H_2S_5O_6 + H_2SO_3$ (D). v is not affected by temp. but is increased by increase in $[H^+]$ and by adding NaCl. At higher temp. reaction (B) also occurs. (II) reacts with $H_2S_2O_3$ according to equation (D). (III) reacts with H_2SO_3 by equation (D) reversed until equilibrium is reached, $[H^+]$ increasing up to this point. Increase in $[H_2SO_3]$ or $[H_2S_2O_6]$ or addition of NaCl all increase the reaction velocity. The remaining (III) is then slowly degraded to (I). (IV) reacts thus: $H_2S_6O_6 + H_2SO_3 \rightarrow H_2S_7O_6 + H_2S_2O_3$ (E). Reactions (C), (D), and (E) are discussed in relation to the Wackenroder reaction.

J. F. H.

Chlorine azide, CIN_3 . I. W. J. Frierson, J. Kronrad, and A. W. Browne. II. Interaction of chlorine azide and silver azide. Azino-silver chloride, N_3AgCl . W. J. Frierson and A. W. Browne (*J. Amer. Chem. Soc.*, 1943, **65**, 1696–1698, 1698–1700).— CIN_3 , prepared by (i) $AgN_3 + Cl_2 \rightarrow AgCl + CIN_3$ and (ii) $HN_3 + HOCl \rightleftharpoons CIN_3 + H_2O$, is a yellow-orange or orange liquid freezing ($\sim -100^\circ$) to an explosive yellow solid. Liquid CIN_3 is not polar and does not act as an ionising solvent. It is slightly sol. in H_2O and readily sol. in C_2H_{10} , C_5H_{12} , C_6H_6 , MeOH, EtOH, Et₂O, COMe₂, $CHCl_3$, CCl_4 , and CS_2 . When gaseous CIN_3 diluted with N_2 is bubbled into excess of NH_3 the reaction $3CIN_3 + 8NH_3 \rightarrow N_2 + 3NH_4Cl + 3NH_4N_3$ occurs quantitatively. When a solution of CIN_3 in anhyd. C_2H_{12} is kept at room temp. in a stoppered vessel for 2 hr. the reaction $CIN_3 + C_2H_{12} \rightarrow HN_3 + C_2H_5Cl$ occurs. Its reactions with metals (Na, Mg, and Zn) and with P are discussed.

II. CIN_3 , in the dry state and in non-aq. solutions, reacts with AgN_3 to yield azino-silver chloride, N_3AgCl , a dark blue solid stable at $<-30^\circ$ but decomp. at higher temp. The following reactions have been observed: $2N_3AgCl + Cl_2 \rightarrow 2CIN_3 + 2AgCl$; $6N_3AgCl + 8NH_3 \rightarrow N_2 + 6NH_4N_3 + 6AgCl$; $2N_3AgCl + SO_2 \rightarrow SO_2(N_3)_2 + 2AgCl$. Tentative suggestions for the mechanism of formation and structure of the compound are advanced.

W. R. A.

Corrosion of iron by ammonia.—See B., 1943, I, 485.

Reduction of potassium cyanopalladate (II) by potassium in liquid ammonia. Zero-valent compound of palladium. J. J. Burbage and W. C. Fernelius (*J. Amer. Chem. Soc.*, 1943, **65**, 1484–1486).— $K_2Pd(CN)_4$ has been prepared by the action of K on $K_2Pd(CN)_4$ in liquid NH_3 . Its properties have been investigated and compared with those of $K_2Ni(CN)_4$. A compound $K_2Pd(CN)_2$ was not obtained.

W. R. A.

Note.—Abstracts of papers on analysis and apparatus will be published in Section C (see Foreword).

X.—LECTURE EXPERIMENTS AND HISTORICAL.

Charles Tennant. (Sir) W. Alexander (*Chem. and Ind.*, 1943, 411–416).

XI.—GEOCHEMISTRY.

Boron in hot springs at Tokaanu, Lake Taupo. J. Healy (*New Zealand J. Sci. Tech.*, 1942, **24**, B, 1–17).—A geological, magnetic, and chemical survey of the area is described. The springs are alkaline and contain large quantities of $Na_2B_4O_7$. The origin of the B is discussed. J. E. P.

Chemistry of lake sediments from Indian Tibet. G. E. Hutchinson, A. Wollack, and J. E. Setlow (*Amer. J. Sci.*, 1943, **241**, 533–542).—Chemical and semi-quant. spectrographic analyses are recorded and discussed. Ca content is correlated with the presence or absence of an outlet. Mg increases only in the sediments of the more conc. closed lakes. Sr appears to follow Ca, but the Sr content is probably also lithologically controlled. Ba is probably sedimented with the silt fraction. The Ca content of the deep- H_2O sediment of Pang-gong Tso has undergone changes; these may be due to a fall in H_2O level. Analyses for CaO and SiO_2 , or a spectrographic comparison of Sr and Ba contents, should reveal periods of high and low levels in the history of a lake. The mean P content of the sediment ash is 0.10%, and loss of P from the H_2O by pptn. as $Ca_3(PO_4)_2$ is of little importance in the economy of even the closed alkaline lakes. The ratio combined N : P varies from 1.7 to 7.8, and the proximate composition of org. matter is essentially that of other harmonic lake sediments. L. S. T.

Chemical composition of Lovozero eudialytites. N. A. Eliseev and E. A. Sverjinskaja (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 244–246).—The eudialytites contain 60–70% of eudialyte. Chemical analyses of 3 different eudialytites are recorded. ZrO, ranges from 6.76 to 8.68%, and $Nb_2O_5 + Ta_2O_5$ from 0.39 to 0.76, with Nb_2O_5 predominating. L. S. T.

Porosity of geospheres. G. A. Maximovitch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **37**, 215–217).—Porosities of strata are calc. from 2572 determinations. F. G. R.

Mineralogy of the Iona [Murmansk] iron ore deposit. G. P. Barsanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 246–250).—Magnetite, forsterite, titanclino-gumite, schorlomite, phlogopite, and staffelite are described, and spectrum analyses recorded.

L. S. T.

Fluorite in the Lower Permian deposits of the Bashkir autonomous Socialist Soviet Republic. V. P. Florenski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 251–254).

L. S. T.

Natural [electrical] potentials in sedimentary rocks. P. A. Dickey (*Amer. Inst. Min. Met. Eng., Tech. Publ.* 1625, 1943; *Petrol. Tech.*, **6**, 10 pp.).—The potential of sandstones and conglomerates is found to be more strongly negative than that of shale. The difference is ascribed to preferential adsorption of ions by the rock materials. A. R. Pe.

Natural [electrical] potentials in [oil] well logging. W. D. Mounce and W. M. Rust, jun. (*Amer. Inst. Min. Met. Eng., Tech. Publ.* 1626, 1943, *Petrol. Tech.*, **6**, 6 pp.).—Electroendosmosis accounts for only a small part of the observed potential variations. When saline (I) and fresh (II) H_2O , separated by a permeable membrane, are brought in contact with shale, an e.m.f. is set up so that current flows through the shale from (I) to (II). These conditions may be provided in a well by the contact of shale, drilling mud, and saline sand. A. R. Pe.

Nephelinised paragneisses of the Bancroft region, Ontario. W. K. Summer and S. V. Burr (*Science*, 1943, **97**, 286–287).—A detailed geological and topographical map of the nepheline-bearing rock east of Bancroft village indicates a parasedimentary origin for the rock. The nepheline content varies both along and across the strike and much of the limestone is classed as “flow marble.” Nephelinisation is probably post-folding. The mechanics of the limestone-syntexis theory are disputed. E. R. R.

New method for studying sandy silt sediments (granulo-morphological analysis). V. P. Baturin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **37**, 66–68).—A survey and discussion of rolling and sliding processes with inclined planes of various materials. N. M. B.

Glauconite deposits in the Novo-Lialin district on the eastern slope of the Urals. S. D. Rabinovitch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **37**, 63–65).—A short survey of the distribution and nature of deposits recently discovered. N. M. B.

Can the “lead method” be used on igneous rocks? F. E. Wickman (*Arkiv Kemi, Min., Geol.*, 1943, **16**, A, No. 23, 9 pp.).—Mathematical. Age determinations can be made on igneous rocks by the Pb method, and unless the different samples of the differentiated rocks show large differences in radioactivity, the method is best used only on pre-Cambrian rocks. The abundance of Pb isotopes at the time of crystallisation can also be calc. L. S. T.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A I—General, Physical, and Inorganic Chemistry.

FEBRUARY, 1944.

I.—SUB-ATOMICS.

Absorption lines of potassium vapour under varying conditions of temperature and pressure. D. K. Bhattacharya and S. P. Sinha (*Indian J. Physics*, 1943, 17, 131—134).—The intensity and no. of lines in the range 4586—2225 Å. of the absorption spectrum of K vapour at 388—695° and 3—400 mm. partial pressure, in K vapour- N_2 mixtures at total pressure 0.1—940 mm., increases with total and partial pressure. L. J. J.

Arc spectrum of oxygen, O I. B. Edlen (*K. Svenska Vet. Akad. Handl.*, 1943, 20, No. 10, 31 pp.).— $\lambda\lambda$ and (visual) intensities of 81 lines (15 new) in O I from 5958 to 9760 Å. have been measured. All lines in the range, excepting the weak multiplet at 8420—8429 Å., are included; older vals. are corr. The whole spectrum has been re-examined and new identifications (43 lines in the long- λ region, and 4 multiplets in the far-ultra-violet) made, including lines corresponding to sp^3P , singlets of $3p$ -configuration, and 28 levels in the $(^2D)nd$ series; previous assignments of the $(^2D)3p^2D$ and $(^2D)3d^2P$ terms are corr. The groups at 9487—9760 Å., 6256—6374 Å., and 5404—5492 Å. are identified as combinations of $(^2D)3p^2F$ and 1F with $(^2D)nd^3G_4$, 3G_4 , and 1G_4 , indicating a selective auto-ionisation effect with extensive disruption of the LS coupling. The complete term system of O I has been recalcd. and tabulated; previous triplet and quintet limits are corr.; the $(-D)$ -singlets now fit accurately into the general framework. The fine structure of $(^4S)3p^2P$ has been worked out, and a small negative splitting demonstrated for $(^4S)nd^2D$ ($n = 3$ and 4). Strong perturbations of $(^4S)np^2P$ by $(^2D)3p^2P$, and of $(^2D)nd^2P$ by sp^3P , have been established and are discussed. The interlinked deep terms s^2p^3P , 1D , and 1S are related to the rest of the term system, permitting very accurate calculation of most lines from 769 to 1358 Å. Slater's method gives accurate calc. terms vals. in the $2s^22p^3s$ and $2s^22p^3p$ configurations. M. H. M. A.

Arc spectrum of tungsten in the ultra-violet. F. Poggio Mesorana (*Anal. fis. quim.*, 1943, 39, 10—20).—In the region 1990—2400 Å., 169 new lines are recorded and some lines previously attributed to other elements are now assigned to W I. F. R. G.

New ultra-violet lines in the spark spectrum of tungsten. F. Poggio Mesorana and J. M. Poggio (*Anal. fis. quim.*, 1943, 39, 21—30).—208 new lines in the 1960—2210 Å. region are recorded. Some of these are assigned to W II, and others to impurities. F. R. G.

Use of iron lines as intensity standards. G. H. Dieke and H. M. Crosswhite (*J. Opt. Soc. Amer.*, 1943, 33, 425—434).—The group of Fe lines between 3140 and 3240 Å. is exhaustively examined and found to be satisfactory for intensity standards for the rapid and reliable calibration of plates. The causes of intensity variation are investigated. In general, the relative intensity of lines of Fe I selected at random is changed much more by self-reversal than by changes in excitation. Conditions for min. self-reversal are given. Weak or moderately strong lines based on all but the lowest levels are free from self-reversal under the usual operating conditions of arcs or sparks. Groups of lines can be chosen so that self-reversal is a function of true intensity only, and conversely, by measuring self-reversal of groups of Fe lines in different regions it is possible to determine their true intensities, and hence the relative intensities of groups in all regions. These groups can be used as standards to eliminate plate sensitivity and instrumental effects when the intensities of widely separated lines are to be measured. The method may be applied to analytical spectroscopy where suitable lines of all the constituents cannot be found close together. A. J. M.

Corona in gases at low pressures. J. D. Craggs and J. M. Meek (*Physical Rev.*, 1943, [ii], 64, 249—250).—A preliminary report of oscillograms obtained at pressures <3 cm. in air, H_2 , O_2 , and CCl_2F_2 . Use of a.c. instead of d.c. has advantages, positive and negative corona, synchronised with the supply voltage, being shown together. A two-beam oscillograph enables tube current to be observed simultaneously with tube voltage or time-calibrating wave. Observations support those of Weissler (cf. A., 1943, I, 173) and show some new effects. N. M. B.

Factors influencing the plateau characteristics of self-quenching Geiger-Müller counters. W. D. B. Spatz (*Physical Rev.*, 1943, [ii], 64, 236—240).—Investigations show that air or O_2 impurities in-
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crease the plateau slope and starting potential of A-alcohol counters. Changes in the plateau and recovery powers of the counter with duration of use are reported. Pressure in an A-alcohol counter increases as a function of the total no. of counts, and the useful life is $\sim 10^2$ — 10^{10} counts; for A- CH_4 , it is 10^7 — 10^8 counts. Changes are attributed to decomp. of org. vapour by the discharge. N. M. B.

β -Ray spectrum of antimony, ^{121}Sb . E. B. Hales and E. B. Jordan (*Physical Rev.*, 1943, [ii], 64, 202—206).—The continuous β -ray spectrum, investigated with a 180° type of spectrometer, consists of two components, the end-points of which are 0.74 ± 0.03 and 2.45 ± 0.07 Me.v. The difference, 1.71 ± 0.03 , agrees with the known val. of the hard γ -ray from ^{121}Sb . In addition, internal conversion lines, corresponding with γ -ray energies of 0.23 and 0.61 Me.v. and probably due to the decay of a long-lived Te isotope present in the source, were observed. A possible energy-level scheme representing this transition is discussed. N. M. B.

Burst production in a gas volume. M. Sinha (*Physical Rev.*, 1943, [ii], 64, 248—249).—A photograph, taken under large thickness of Pb, of a burst inside a Wilson chamber is discussed. Possible explanations of the origin of the burst are considered. N. M. B.

Multiple production of secondary cosmic-ray particles in the lower atmosphere. V. H. Regener (*Physical Rev.*, 1943, [ii], 64, 250—252).—With an arrangement of 125 counter tubes above and between 6 layers of Pb, investigations were made at altitudes sea level—14,000 ft. A study of 200,000 photographs shows two processes of production of secondary particles: in the first, a neutral radiation produces in the 1-cm. top layer of Pb single non-multiplying particles, mostly of range <5 cm. Pb (cf. following abstract); in the second, the particles produced invariably come in showers, 0.1 of the observed production processes being initiated by penetrating ionising rays, and 0.9 by penetrating non-ionising rays. Data for cross-sections of processes, particle range, and altitude dependence of production are briefly indicated. N. M. B.

Absorption curve and production of slow cosmic-ray protons at low altitude. V. H. Regener (*Physical Rev.*, 1943, [ii], 64, 252—253; cf. preceding abstract).—An absorption curve of the non-cascade-forming particles produced by a non-ionising radiation is given and discussed. The particles are identified with the protons reported by Powell (cf. A., 1942, I, 312). N. M. B.

Production of secondaries in paraffin by primary cosmic-ray particles. M. Schein, M. Iona, jun., and J. Tabin (*Physical Rev.*, 1943, [ii], 64, 253—254).—Balloon experiments at high altitudes (5—17 cm. Hg pressure) show that a large fraction of the penetrating ionising rays are accompanied by secondaries produced in the paraffin. The approx. cross-section for production is $\sim 10^{-24}$ sq. cm. There is evidence that the primaries are protons, and the decrease in intensity at decreasing altitudes gives an absorption cross-section of 2×10^{-23} sq. cm., or approx. the area of a N or O nucleus. N. M. B.

Origin of large bursts under thick shields. R. E. Lapp (*Physical Rev.*, 1943, [ii], 64, 254—255).—Experiments with a high-pressure ionisation chamber, shielded by 35 cm. of Fe, to record cosmic-ray bursts containing >100 particles show that the bursts are produced mainly by mesotrons, and that only 4—7% of the bursts are due to atm. showers (cf. A., 1944, I, 2). N. M. B.

Spin of the mesotron from burst measurements. R. E. Lapp (*Physical Rev.*, 1943, [ii], 64, 255—256).—A size-frequency distribution curve for bursts in an ionisation chamber under 10.7 cm. Pb shielding is compared with the theoretical curves for bursts produced by mesotrons of spin 0, $\frac{1}{2}$, and 1 (cf. Christy, A., 1941, I, 235). Very close agreement with the theoretical curve for spin 0 is shown, but the possibility of spin $\frac{1}{2}$ is discussed (cf. following abstract). N. M. B.

Effect of radiation damping on burst production. S. Kusaka (*Physical Rev.*, 1943, [ii], 64, 256—257).—Possible causes of differences in the calculations and results of Christy (cf. A., 1941, I, 235) and Chakrabarty (cf. A., 1943, I, 247) are discussed; the findings by the latter of meson spin 1, but not 0 or $\frac{1}{2}$, are discredited. N. M. B.

Multiple production of penetrating particles by cosmic-ray protons and neutrons. W. E. Hazen (*Physical Rev.*, 1943, [ii], 64, 257).—Experiments showed no direct evidence for a cascade production of
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mesotrons in close nuclear encounters by protons or neutrons as calc. by Hamilton (cf. A., 1944, I, 2), but several cases of multiple production of energetic penetrating particles in a single event have been photographed. N. M. B.

Disintegration curve of mesotrons. N. Nereson and B. Rossi (*Physical Rev.*, 1943, [ii], 64, 199—201; cf. A., 1943, I, 79).—Extensive further measurements summarised and plotted give $2.15 \pm 0.07 \mu\text{-sec.}$ for the mean life, as calc. from the differential disintegration curve. N. M. B.

Scattering of mesons under the influence of radiation damping. S. T. Ma (*Proc. Camb. Phil. Soc.*, 1943, 39, 168—172).—Exact solutions of the relativistic equations for the scattering of a positive meson by a neutron and of a negative meson by a proton, radiation damping being taken into account, lead to vals. of the cross-sections very close to those obtained by Heitler (A., 1941, I, 291) for the non-relativistic approximation. It is suggested that non-relativistic calculations should also give correct results for the scattering of positive and negative mesons by protons and neutrons, respectively, for which processes the relativistic theory is more difficult. H. J. W.

Algebra of meson matrices. N. Kemmer (*Proc. Camb. Phil. Soc.*, 1943, 39, 189—196).—The algebra normally used in meson theory, defined by the relation $\beta_\lambda \beta_\mu \beta_\nu + \beta_\nu \beta_\mu \beta_\lambda = \beta_\lambda \delta_{\mu\nu} + \beta_\nu \delta_{\mu\lambda}$, and in which only four β elements exist, is extended to cover the existence of any no. of elements. Expressions are deduced for the no. of linearly independent elements, for the no. of algebraically independent irreducible representations, and for their ranks. A method is given for constructing these representations. H. J. W.

Statistical mechanics of processes observed in cosmic-ray phenomena. G. Wataghin (*Physical Rev.*, 1943, [ii], 64, 248).—Mathematical. In processes involving emission of neutrinos an appreciable fraction of the successively transformed energy of a primary particle escapes observation, and the statistical laws for such processes differ from the usual ones. A modification of the usual statistical laws is outlined. N. M. B.

Theory of spin of elementary particles. V. L. Ginzburg (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 319—323). A. J. M.

The hydrogen atom and the classical theory of radiation. C. J. Eliezer (*Proc. Camb. Phil. Soc.*, 1943, 39, 173—180).—The equations of motion of an electron in an external electromagnetic field (using Dirac's relativistic theory) are considered. For an electron moving in a straight line towards a fixed proton or towards another electron, and for the three-dimensional motion around a fixed proton, there appear to be no solutions corresponding with an actual collision. H. J. W.

Interaction of two point charges. E. A. Milne (*Phil. Mag.*, 1943, [vii], 34, 712—716).—A simplified derivation of the energy and angular momentum integrals for a pair of point charges, using τ -measures instead of the t -measures used previously (cf. A., 1943, I, 141). H. J. W.

II.—MOLECULAR STRUCTURE.

Spectrum physics and thermodynamics. Calculation of free energy, entropy, specific heat, and equilibria from spectroscopic data, and the validity of the third law. H. Zeise (*Z. Elektrochem.*, 1941, 47, 595—617). J. H. BA.

Absorption spectrum of nitrogen in the extreme ultra-violet. R. E. Worley (*Physical Rev.*, 1943, [ii], 64, 207—224).—Investigations, at large dispersion, of the spectrum corresponding with excited states in the range 12.2—17.0 e.v. give data tabulated for an extensive Rydberg series of bands. The ionisation potential of N_2 corresponding with the series limit is 15.577 v. Interpretation of results and evaluation of consts. are given and discussed. N. M. B.

Band spectrum of phosphorus. I. Rotational structure. II. Alternating intensity and nuclear spin. K. N. Rao (*Indian J. Physics*, 1943, 17, 135—140, 149—152).—I. The bands (9, 21), (5, 21), (5, 18), and (4, 18) of P_2 vapour excited in a discharge tube have been measured. Rotational consts. found are: B'_4 0.2346, B'_5 0.2323, B'_6 0.2255, B'_{18} 0.2799, B'_{21} 0.2736. No rotational perturbations are found. Those reported by Herzberg (A., 1933, 199) must be vibrational.

II. The alternating intensity in the rotational structure of the (5, 21), (5, 18), (9, 21), and (6, 22) bands of P_2 has been measured. All except the (5, 21) band give an intensity ratio 3.0; the (5, 21) band gives 3.3. The anomaly is not due to perturbations. A val. $\frac{1}{2}$ is found for the nuclear spin quantum no. for P. L. J. J.

Intensity distribution in molecular spectra: class I systems of mercurous chloride and mercurous bromide. M. G. Sastry (*Indian J. Physics*, 1943, 17, 141—148).—Peak intensities for bands of the $Hg^{2+}Cl$ and $Hg^{2+}Br$ (class I) systems at 2650—2400 Å. have been determined by the slit-width method. Transition probabilities and effective temp. are calc. L. J. J.

Intensity of solar radiation in the Arctic. N. N. Kalitin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 329—332).—There is a min. in the intensity of solar radiation in the summer months, and a max. in the winter. This is attributed to changes in H_2O vapour concn. in the atm. A. J. M.

Ultra-violet absorption spectra of arylethylenes. R. N. Jones (*J. Amer. Chem. Soc.*, 1943, 65, 1818—1824).—The ultra-violet absorption spectrum of tetra-(9-phenanthryl)ethylene in EtOH-dioxan has been investigated and compared with that of 4*M*-phenanthrene. Substances having the formula $CRR'R''R'''$ ($R, R', R'',$ and $R''' = H$ or Ph) give spectra resembling those of either styrene or *trans*-stilbene, *cis*-stilbene being the sole exception. This behaviour is explained by steric considerations. W. R. A.

Ultra-violet absorption spectra of derivatives of chrysene. R. N. Jones (*J. Amer. Chem. Soc.*, 1943, 65, 1815—1818).—The ultra-violet absorption spectra of 6-isopropenyl- (I), 6-acetyl-, isomeric acetyl-, and diacetyl-chrysene have been measured. The similarity between the spectra of (I) and 6-methylchrysene is attributed to steric effects which prevent the C:C group from acquiring a configuration coplanar with the chrysene ring system; consequently, interaction between the aromatic ring and the C:C linking does not occur. W. R. A.

Effect of molecular environment on the absorption spectra of organic compounds in solution. III. Compounds containing the chromophore :C:C:C:N. L. K. Evans and A. E. Gillam (*J.C.S.*, 1943, 565—571).—The absorption spectra of oximes, semicarbazones, methylsemicarbazones, and thiosemicarbazones of a no. of saturated aldehydes and ketones and $\alpha\beta$ -unsaturated aldehydes, in EtOH solution, are recorded. The thiosemicarbazones of saturated aldehydes and ketones have absorption bands at ~ 2700 Å., ~ 500 times as intense as those of the parent $\cdot CO \cdot$ compounds, and provide a method of detecting isolated $\cdot CO \cdot$ groups. L. J. J.

Lignin and related compounds. LXXII. Ultra-violet absorption spectra of compounds related to lignin. R. F. Patterson and H. Hibbert (*J. Amer. Chem. Soc.*, 1943, 65, 1862—1869; cf. A., 1943, II, 347).—Ultra-violet absorption spectra in EtOH are recorded for 42 compounds of the types, $ArOH$, $ArOMe$, $CHAr:CHMe$, $CH_2Ar:CH:CH_2$, $COR:CHMe:OH$, $OH:CHAr:COMe$, $ArCHO$, and $CH_2Ar:OH$, in which $Ar = 3:4:1-OH:C_6H_3(OMe)_2$ and $-(OMe)_2C_6H_3$, $3:4:5:1-(OMe)_2C_6H_3$, and $4:3:5:1-OH:C_6H_3(OMe)_2$. Max. are recorded in Fresnel units (f) [$= 0.03 \nu$ (cm.⁻¹)]. Compounds containing $3:4:1-OH:C_6H_3(OMe)_2$ or $-(OMe)_2C_6H_3$ conjugated with unsaturation in the C_3 -side-chain have max. at 980 f due to the conjugated unsaturation, 1070 f due to the free m -position, and 1300 f due to an unexplained characteristic of the aromatic nucleus. The m -position is not free in compounds containing $4:3:5:1-OH:C_6H_3(OMe)_2$, similarly conjugated, which accordingly have max. only at 980 and 1300 f . Similar compounds containing $3:4:5:1-(OMe)_2C_6H_3$ have max. at 1070 and 1300 f , the 980 f max. having suffered a shift of 80—90 f . Methylation of the phenolic OH slightly decreases the extinction at 980 f in both series, but the 1300 f max. is probably unaffected. The 980 f band due to conjugation affords a clear distinction between $CH_2:CHMe$ and allyl, $CO:CHMe:OH$ and $OH:COMe$, or CHO and $CH_2:OH$. R. S. C.

Dependence of fluorescence efficiency of solutions on the wavelength of the exciting light. S. S. Solomin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 742—746).—Vavilov's rule that the quantum efficiency of fluorescence is const. up to a crit. λ , and then falls off rapidly to zero, has been verified experimentally for 14 org. substances. A. J. M.

Effect of naphthalene on the fluorescence of hydrocarbons. J. A. Miller and C. A. Baumann (*Cancer Res.*, 1943, 3, 217—222).—Details are given for the purification of carcinogenic and related hydrocarbons, for the quant. determination of fluorescence in liquid solution, and for the photography of the fluorescence spectra of these hydrocarbons in solution and in the solid state. 0.1% solid solutions of naphthalene (I) in 3:4-benzpyrene (II), 20-methylcholanthrene, 9:10-dimethyl-1:2-benzanthracene, 1:2-benzanthracene, or in anthracene show fluorescence bands, which differ from those of either component and appear to be characteristic of the fluorescence of (I) in solid hydrocarbon solutions. The solid hydrocarbons and their solid solutions with (I) lose their ability to fluoresce on fusion in air or in vac. and regain it on resolidification. (II), when heated in liquid solution to its m.p., retains its fluorescence. (I) does not inhibit the fluorescence of liquid solutions of the hydrocarbons. F. L. W.

Factors that alter the fluorescence of certain carcinogens. J. A. Miller and C. A. Baumann (*Cancer Res.*, 1943, 3, 223—229).—The intensity of fluorescence in solution has been measured for 7 hydrocarbons in 37 solvents. In most solvents fluorescence increases progressively in the order: naphthalene, 1:2:5:6-dibenzanthracene (I), 1:2-benzanthracene, anthracene, 9:10-dimethyl-1:2-benzanthracene, 20-methylcholanthrene, 3:4-benzpyrene. Fluorescence is most intense in tetrahydrofurfuryl alcohol, C_6H_5N , $OH[CH_2]_2OMe$, and dioxan; it is low in the lower alkanes, and zero in CS_2 or NH_3Ph . The fluorescence of these hydrocarbons, with the

exception of (I), is partly destroyed in solution by prolonged exposure to ultra-violet. Each hydrocarbon is stable to refluxing in 10% alcoholic KOH for 1 hr. The most potent inhibitor of fluorescence is $C(NO_2)_4$. The inhibition is irreversible. The fluorescence of the unsaponifiable matter of mouse tissue is measured in 18 solvents. The fluorescence is very weak as compared with that of the hydrocarbons and does not vary greatly with solvent. In mixtures it is strictly additive to the hydrocarbon fluorescence. F. L. W.

Method for determining depolarisation factors in Raman spectra.—See C., 1944, Part 1.

Normal vibrations and structure of germanium hydride. K. Schäfer and J. M. Gonzalez Barredo (*Anal. fts. quim.*, 1943, **39**, 297—305).—The Raman spectrum of GeH_4 confirms its tetrahedral structure. Calc. force consts. correspond with an intermediate mol. model. F. R. G.

Raman spectrum of O-methylisourea hydrochloride. J. T. Edsall (*J. Amer. Chem. Soc.*, 1943, **65**, 1814—1815).—The Raman spectrum of $OMe \cdot C(NH_2)_2^+ Cl^-$ in H_2O is essentially the spectrum of the cation, which is similar to the methylguanidinium ion. W. R. A.

Molecular complexity of some gases in the high-frequency discharge. H. O. McMahon and M. J. Marshall (*Trans. Electrochem. Soc.*, 1943, **84**, Preprint 24, 255—266).—An equation is obtained giving the degree of dissociation of a gas when subjected to a high-frequency discharge, as a function of the temp. gradient of the fractional increase of pressure (p) caused by the discharge, corr. for the effect of temp. on the thermal conductivity of the gas. The increase of p was determined for H_2 , A, and H_2 -A mixtures on passage of a discharge at various temp. Results indicate that H_2 is <0.5% dissociated. In a H_2 -A mixture containing 46.8% of H_2 , 2.6% of the H_2 is dissociated, and in a mixture containing 9.2% of H_2 , 76% is dissociated. N_2 and O_2 , present as impurities in the A, are almost completely dissociated by the discharge. The dissociation of a polyat. gas mixed with A increases with decrease in its concn. in the mixture. The instantaneous increase of p observed when the discharge is passed through a gas is largely due to the heating of the gas. A. J. M.

Hyperconjugation in methylbutadienes as shown by dipole moments. N. B. Hannay and C. P. Smyth (*J. Amer. Chem. Soc.*, 1943, **65**, 1931—1934).—Vals. of μ are given for butadiene 0, α - (trans) 0.68, and β -methyl- 0.38, and β -dimethyl-butadiene (I) 0.52 D. Mols. of (I) are predominantly in a *cis*-form with respect to the central C-C linking. The vals. support hyperconjugation. W. R. A.

Dipole moments of the chief constituents of lac and rosin. G. N. Bhattacharya (*Indian J. Physics*, 1943, **17**, 153—161).—Dipole moments found for abietic acid, soft lac resin, and pure lac resin, in dil. dioxan solutions at 25°, are 1.35, 4.61, and 7.45 D., respectively. L. J. J.

Effect of various organic radicals on the atomic refractivities of the halogens. W. K. Plucknett (*Iowa State Coll. J. Sci.*, 1943, **18**, 77—79).—Vals. of b.p. or m.p., n_D^{20} , n_D^{25} , $[R]_D$, $[R]_{25}$, and at. dispersion are recorded for C_2H_5 , $PhMe$, PhX , p - C_6H_4MeX , $PhNO_2$, $BzCl$, $BzBr$, n - C_4H_9 , n - C_4H_9Br , n - $C_7H_{15}I$, and solutions (mol. fractions 0.2 and 0.4) of $PhNO_2$ and o - and m - $C_6H_4X \cdot NO_2$ in dioxan ($X = Cl, Br, I$). The at. refractivity of the halogen decreases in the following order of attached groups: Bz , p - C_6H_4Me , Ph , n - C_4H_9 . No correlation is observed between at. refractivity and electron-sharing capacity, electronegativity, mol. wt., or reactivity; at. refraction is attributed to a complex combination of forces. A. J. E. W.

Molecular arrangement in high-polymeric substances. Optical double refraction, chemical structure, and orientation in substances with felted and netted molecules. F. H. Muller (*Angew. Chem.*, 1940, **53**, 425—428).—Optical anisotropy arises when the random arrangement of mols. is modified, e.g., by application of an electric field (Kerr effect). High-polymeric substances become double-refracting when subjected to mechanical deformation. The double refraction is related to the relative extension and the polarisabilities of the monomer. Proportionality between the tension in stretched materials and the double refraction is deduced, and confirmed experimentally for polystyrene and polyvinyl chloride. Branching and netting of chains does not substantially alter the results. The relations do not hold if crystallites or micelles are present or are formed on stretching. The significance of double refraction as a measure of mol. arrangement in practical problems is indicated. R. H. F.

Absorption of light by small drops of water. R. Ruedy (*Canad. J. Res.*, 1943, **21**, A, 79—88).—The effect of drop size on the extinction coeff. (k) of H_2O particles in and near spectral regions of strong absorption is calc. by means of Mie's theory. k is < the val. for perfectly transparent particles when λ is < the radius of the particles, the change in k being > 10%, and negligible when λ is < 1 μ . The main features of the scattering are unchanged by absorption. L. J. J.

Valency-force model and dissociation of polyatomic molecules. M. Wehrli and G. Milazzo (*Helv. Chim. Acta*, 1943, **26**, 1025—1033).—Differences between the bond energies for individual linkings and B 2 (A., 1.)

the dissociation energies for triat. mols. are due to electron shifts. Under suitable conditions, vals. for the bond energy and the elastic const. for a particular linking in one mol. may be assigned to the corresponding linking in another mol. The dissociation energies for the splitting-off of the heavier halogen atom (from fluorescence spectra) for $HgClBr$ and $HgBrI$ are 69.6 and 63.5 kg.-cal. per g.-mol. F. J. G.

Momentum distribution in molecular systems. VII. Momentum distribution and shape of the Compton line for Li_2 and N_2 . W. E. Duncanson (*Proc. Camb. Phil. Soc.*, 1943, **39**, 180—188).—For Li_2 the radial momentum distribution and the Compton profile are calc., using three types of wave-function. For N_2 the wave-function used is of the Fock type, with exponents slightly different from Slater's. There is a considerable discrepancy between theory and experiment for the Compton profile for N_2 , possibly due in part to the inexact wave-function and in part to uncertainties in the experimental results. (Cf. A., 1942, I, 134.) H. J. W.

Definition of surface tension.—See A., 1943, I, 303.

Contact angles.—See A., 1943, I, 303.

Relation between surface tension and vapour pressure of liquids.—See A., 1943, I, 304.

Surface tension of oils containing dissolved gases.—See B., 1944, I, 10.

III.—CRYSTAL STRUCTURE.

Diffraction of X-rays by binary alloys. R. Smoluchowski (*Physical Rev.*, 1943, [ii], **64**, 257—258).—Mathematical. N. M. B.

Width of X-ray diffraction lines from cold-worked tungsten and α -brass. C. S. Smith and E. E. Stickley (*Physical Rev.*, 1943, [ii], **64**, 191—198).—Measurements as a function of Bragg angle and X-ray λ agree with the micro-stress theory of broadening. In α -brass, but not in W, the line width depends in a systematic manner on crystallographic direction. Observations are explained on the elastic properties of the materials. N. M. B.

Relation between the external form of sucrose crystals, homogeneity, and supersaturation. N. N. Scheftal (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 33—36).—Experiments on the growth of sucrose crystals from pure solution are described. The close relationship between the external form of the crystals and their homogeneity, and the dependence of these properties on very small changes in concn. in the neighbourhood of saturation, are detailed. L. S. T.

Arrangement of double molecules on a lattice. S. K. Kao and T. S. Chang (*Trans. Faraday Soc.*, 1943, **39**, 288—294).—Mathematical. The validity of the approx. formula obtained previously (A., 1939, I, 315) is investigated. F. L. U.

Crystal structure of Pb_3O_4 and $SnPb_3O_{10}$. A. Byström and A. Westgren (*Arkiv Kemi, Min., Geol.*, 1943, **16**, B, No. 14, 7 pp.).— Pb_3O_4 is tetragonal with a 8.80, c 6.66 Å, agreeing with Straumanis (A., 1943, I, 83). There are 4 Pb_3O_4 mols. in the unit cell. The structure corresponds with that of antimonites such as $ZnSb_2O_7$. $SnPb_3O_{10}$, the only compound of this type that could be obtained, has a 8.72, c 6.30 Å. A. J. M.

Crystal structure of $AlCuMg$. H. Perlitz and A. Westgren (*Arkiv Kemi, Min., Geol.*, 1943, **16**, B, No. 13, 5 pp.).—The crystals are orthorhombic with a 4.00, b 9.23, c 7.14 Å; 16 atoms per unit cell. A. J. M.

Structure of rhombic thallous nitrate. L. Rivoir and M. Abbad (*Anal. fts. quim.*, 1943, **39**, 306—331).—Rhombic $TlNO_3$ probably belongs to the crystal class D_2^2 having a 6.17, b 12.27, c 3.98 Å, 4 mols. per cell. F. R. G.

Structure of martensite. H. Lipson and (Miss) A. M. B. Parker (*Iron and Steel Inst.*, Nov. 1943, *Advance copy*, 13 pp.).—Martensite may be considered as ferrite supersaturated with C. Measurements of the intensity ratios of the X-ray line doublets given by the tetragonal structure suggest that the Fe atoms may be displaced from the corners and centres of the unit cell by different amounts in different parts of the same crystal. As a consequence, sufficient of the octahedral interstices are enlarged to accommodate the C atoms. J. C. C.

X-Ray diffraction of sodium laurate, palmitate, and stearate at room temperature. J. W. McBain, O. E. A. Bolduan, and S. Ross (*J. Amer. Chem. Soc.*, 1943, **65**, 1873—1876).—Fibre and powder photographs of Na laurate, palmitate, and stearate confirm the unit cell of β -monoclinic soap and give the unit cell for a "hydrated γ -form" of monoclinic soap at room temp. α -, β -, and γ -forms differ primarily in long spacings and to a smaller extent in lines corresponding with side spacings. In the powder diagram the strongest characteristic β -line corresponds with $d/n = 4.28$ Å, whereas that of the γ -phase is $d/n = 4.00$ Å. W. R. A.

Solid soap phases.—See A., 1943, I, 306.

Crystal structure of the low-temperature form of abietic acid. H. S. Shdanov, M. J. Lazarev, and N. G. Sevastianov (*Compt. rend.*

Acad. Sci. U.R.S.S., 1941, **31**, 767—768).—Abietic acid is monoclinic and has a 11.7, b 11.6, c 14.1 Å; β 112°; V 1780 cu. Å; ρ 1.132; 4 mols. in unit cell; probable space-group C_2^2 . A. J. M.

Axial lengths of phloroglucinol dihydrate crystals. C. R. Bose and R. Sen (*Indian J. Physics*, 1943, **17**, 163—165).—Rotation and oscillation X-radiograms give a 6.740, b 8.090, c 13.604 Å. Goniometric measurements give $a:b:c = 0.8324:1:3.366$. $\rho = 1.453$. L. J. J.

Structure of rubber.—See A., 1943, I, 306.

Electron diffraction study of hydrogen peroxide and hydrazine. P. A. Giguère and V. Schomaker (*J. Amer. Chem. Soc.*, 1943, **65**, 2025—2029).—Diffraction patterns for N_2H_4 show no evidence for dimerisation and give N—H distance as 1.04—0.06 Å. and angle H—N—H as $108 \pm 10^\circ$. For H_2O_2 a new Pyrex nozzle is used; decomp. at $\sim 140^\circ$ is inhibited by small quantities of $NaPO_3$ solution; the O—O distance is 1.47 ± 0.02 Å. W. R. A.

Visual investigation of glycogen molecules. E. Husemann and H. Ruska (*J. pr. Chem.*, 1940, [ii], **156**, 1—10).—Two specimens of glycogen, mol. wts. 1.5×10^6 and 6.5×10^4 , have been investigated with the electron microscope. The mol. is spherical, confirming the evidence of measurements of η and π and explaining the form of the evaporation figures. Mol. diameter calc. from the mol. wt. agrees well with the photographic val. W. R. A.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Physical constants of butadiene and styrene. C. A. Wood and C. F. Higgins (*Petrol. Refiner*, 1943, **22**, 87—88).—A review.

Molecular concept in micro- and macro-molecular chemistry. H. Staudinger (*J. pr. Chem.*, 1940, [ii], **156**, 11—26).—A review. "Physical" and "chemical" mols. are defined, and discussed with particular reference to colloidal and macromol. substances. W. R. A.

Macromolecular structure of lichenin. H. Staudinger and B. Lantzsch (*J. pr. Chem.*, 1940, [ii], **156**, 65—96).— η , π , and $[\alpha]_D^{20}$ of lichenin (I), its acetates (II), and nitrates have been determined in various solvents. Mol. wts., η_{sp} , and K_m consts. have been calc. Mol. wt. determinations on the original (I) and on that recovered from (II) by hydrolysis prove that lichenin is macromol. and not colloidal. Vals. of K_m are consistent with an elongated mol., somewhat shorter than a cellulose mol. of the same degree of polymerisation. Whether branching or twisting of the mol. causes this shortening cannot be decided. W. R. A.

Determination of mol. wts. by dialysis.—See A., 1943, I, 304.

Thermal and electrical conductivities of tungsten and tantalum. (Miss) M. Cox (*Physical Rev.*, 1943, [ii], **64**, 241—247).—Since available data are exiguous and conflicting, an investigation was made of the variation with temp. of the resistance, thermal conductivity, and Wiedemann-Franz ratio of pure W and Ta wires at 77—373° K. A method of calculating the thermal conductivity from the resistance at zero power-input and the slope of the resistance-power-input curve is developed. Limitations of the method lead to inconclusive results. An anomaly in the variation with temp. of the resistance of Ta was observed. N. M. B.

Critical fields of superconductive vanadium. N. E. Alexeevski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 327—328).— V shows very high vals. for the crit. field. $dH/dT = 2400$ Gauss per degree, a val. which is that for any other superconductive metal. The crit. temp. obtained by extrapolation is 4.73° K., which is somewhat > the val. obtained by Meissner *et al.* (A., 1934, 246). A. J. M.

Properties of low-reflexion films produced by the action of hydrofluoric acid vapour. F. H. Nicoll and F. E. Williams (*J. Opt. Soc. Amer.*, 1943, **33**, 434—435).—Glass exposed to vapour from dil. HF is covered with a white deposit, which is sol. in H_2O . When this is removed, a hard, insol., low-reflexion film remains. Such films are produced only in a relatively narrow concn. range, and consist of skeletonised SiO_2 . The method can be used with any type of glass, and produces a film which is more durable than the best evaporated films. The film is highly resistant to abrasion, and the very low scattering makes it useful where good transmission is required (cf. C, 1944, Part 1). A. J. M.

Heat of formation of iron disulphide.—See A., 1943, I, 308.

Thermal properties of isopentane. J. G. Aston (*J. Amer. Chem. Soc.*, 1943, **65**, 2041).—Anomalies found by Guthrie and Huffmann (A., 1943, I, 253) are attributed to inherent differences in methods of measurement. W. R. A.

Determination of thermal and calorific properties of difluoromono-chloroethane. L. Riedel (*Z. ges. Kälte-Ind.*, 1941, **48**, 105—107; *Chem. Zentr.*, 1942, I, 738).—Determinations of the sp. vol. of the liquid between -79.6° and 30.1° , of the equation of state of the vapour, of the v.p. curve, and of the sp. heat of the liquid in the

saturated state were made on pure $CMcF_2Cl$, and the enthalpy and entropy of the saturated liquid were calc. The normal b.p. was calc. as -9.21° . The heat of vaporisation was calc. with the aid of the Clausius-Clapeyron equation. R. B. C.

Physical states of anhydrous sodium soaps. W. Gally and I. E. Puddington (*Canad. J. Res.*, 1943, **21**, B, 202—210).—Cooling curves for Na stearate and oleate show for the former a unidimensional m.p. at 70° , a phase transition, probably due to melting in a second direction at right angles to the mol. axis, at $\sim 100^\circ$, and a further transition at 125 — 130° leading to a plastic state corresponding to complete two-dimensional melting. The next phase change is at 200° , giving the liquid crystal, with probable disruption of the polar linkages. Only the latter transition, at $\sim 135^\circ$, is found with Na oleate. L. J. J.

Effect of certain addition agents on the physical states of sodium soaps. W. Gally and I. E. Puddington (*Canad. J. Res.*, 1943, **21**, B, 211—218).—Non-polar mineral oils, e.g., those of high η index, have no effect on the density-temp. curves of Na stearate and oleate. Glycerol and polar oils of low η index have no effect up to the unidimensional m.p. at 70° for Na stearate, but markedly lower transition points and m.p. at higher temp., particularly above the plasticity points. The presence of free alkali does not influence the effects. L. J. J.

Pressure-volume-temperature relations of $\beta\beta$ -dimethylbutane. W. A. Felsing and G. M. Watson (*J. Amer. Chem. Soc.*, 1940, **62**, 1889—1891).— p - v - θ relations of $EtBu^u$ are determined at 25° intervals from 100° to 275° at pressures from 1 to 2 atm. > v.p. to ~ 300 atm. Sp. vols. are related to pressures at different temp. W. R. A.

Form of condensed water vapour on metal surfaces at low temperatures, below 0° . V. A. Bazikailo (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 333—334).—When a polished metal surface is cooled well below 0° in an atm. containing H_2O vapour, drops of H_2O form and disappear again on cooling through a further 0.1 — 0.2° . At lower temp. ($< -20^\circ$) there is occasional spontaneous formation of the solid from the liquid phase, though this occurs only on definite small areas of the surface. If the condensate is in contact with light objects, such as cotton wool, the original liquid phase always passes into the solid. A. J. M.

Nomograph of Dittus-Boelter equation. C. J. Ryant, jun. (*Ind. Eng. Chem.*, 1943, **35**, 1187—1188).—A nomograph of the equation $h = 0.0243(k/D)(Du\rho/\eta)^{0.3}(\mu C_p/k)^{0.4}$ (h = coeff. of heat transfer, k = thermal conductivity, D = characteristic length of pipe in which turbulent flow is occurring, u = linear velocity) has been constructed and is reproduced. C. R. H.

Dynamic viscosity of nitrogen. W. L. Sibbitt, G. A. Hawkins, and H. L. Solberg (*Trans. Amer. Soc. Mech. Eng.*, 1943, **65**, 401—405).—A Ni capillary 118 ft. long was used in the investigation. Data are reported for 45 calibration tests and 395 tests on N_2 up to 1020 lb. per sq. in. and 496° . An equation which expresses the results is presented. R. B. C.

Viscosity of substances in liquid and gaseous state. Measurement of viscosity of liquid nitrogen. W. Fritz and J. Hennenhofer (*Z. ges. Kälte-Ind.*, 1942, **49**, 41—46; *Chem. Zentr.*, 1942, II, 1211).—The relation of η for the liquid and saturated vapour states at a given temp. can be expressed by the same curve for CO_2 , SO_2 , NH_3 , and $MeCl$. If the η is known for one state it can be calc. approx. from the curve for the other state. The η of liquid N_2 (96% pure) was determined at 77.7° K.; the val. for the gaseous state determined from the curve agrees with the val. determined by other methods. R. B. C.

Size of gas bubbles. I. Evolution from a single capillary. II. Evolution from filter-plates. A. Guyer and E. Peterhans (*Helv. Chim. Acta*, 1943, **26**, 1090—1107, 1107—1113).—I. The diameter (D) of gas bubbles from a single capillary in various liquids depends chiefly on η for the liquid, γ , and the diameter (d) of the capillary, according to $D = [K_1\gamma + K_2 \log \eta + K_3 d^{1/3}]$, where the consts. K_1 , K_2 , and K_3 have empirical vals. 0.012, 0.07, and 1.90, respectively.

II. The diameter (D) of gas bubbles from filter-plates in various liquids increases with increase of γ , streaming velocity, and pore diameter. With increasing η , D first falls to a min. and then increases. F. J. G.

Gas-dynamical contribution to the evaluation of flame experiments in tubes. G. Damkohler and A. Schmidt (*Z. Elektrochem.*, 1941, **47**, 547—567).—By the use of a one-dimensional treatment of streaming processes, relations are obtained between pressure (p), sp. vol., temp., mean streaming velocity, and position along the tube for a gas flowing along a straight tube. These are derived for a primary percussion wave in front of a piston moving with const. velocity (corresponding with a flame front of const. velocity), the reflexion of the wave from a rigid wall, the wave at the open end of a tube, and in the wave front of an accelerating piston (corresponding with an accelerating flame). Curves of p , temp., and d changes with distance, for known flame or percussion wave velocities, and for

various vals. of the isentropic exponent, are given, and can be used in the evaluation of flame or schlieren photographs. J. H. Ba.

Viscosity and working properties of glass.—See B., 1944, I, 23.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Ultrasonic wave velocity in aqueous mixtures of some organic liquids. I. G. Michailov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 324—326).—The velocity of ultrasonic waves in aq. solutions of MeOH, EtOH, COMe₂, AcOH, and C₂H₅N, and in NH₂Ph-AcOH mixtures has been determined. Aq. solutions of MeOH, EtOH, and COMe₂ fall into one class, in which d varies almost linearly with concn. and the velocity of sound is a max. at ~30% concn. for all these solutions. The max η also occurs for these solutions in the range 40—50%. AcOH-H₂O has a max. d and η at a concn. of 80%, and max. velocity of sound at 20%. For C₂H₅N-H₂O, max. velocity occurs at 60%, and coincides approx. with max. d and η . For NH₂Ph-AcOH there is a max. d at 70%, and max. η at 60%, but no velocity max. A. J. M.

Ultrasonic wave velocity in formic acid-water mixtures. I. G. Michailov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 550—552).—At concns. of 1 mol. HCO₂H to 1 mol. H₂O, and 1 mol. HCO₂H to 2 mols. H₂O, there are definite changes in ultrasonic velocity, the effect being greater for the first mixture than for the second. Similar changes in d , η , and other properties have also been observed at these concns. The velocity-concn. curve shows a max. at a concn. of ~20% HCO₂H. A. J. M.

Dependence of fluorescence efficiency of solutions on the wavelength of exciting light.—See A., 1944, I, 28.

Kinetics of recrystallisation process. K. S. Lialikov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 585—587).—The applicability of Smoluchowsky's equation to recrystallisation under conditions eliminating coagulation has been investigated. Four series of NH₃ photographic emulsions were used, the recrystallisation of AgBr being determined for different solubilities, various concns. of KBr being present. Smoluchowsky's equation holds approx., the discrepancy being ascribed to the presence of different quantities of complex compounds. A. J. M.

Molal depression constant for camphor. W. B. Meldrum, L. P. Saxer, and T. O. Jones (*J. Amer. Chem. Soc.*, 1943, **65**, 2023—2025).—The val. of K for camphor has been determined using different concns. of C₁₀H₈, *p*-C₆H₄PhBr, CH₂Ph-CO₂H, and NPhEtAc. At >0.2M. K has a const. val. of 39.7° per kg., but at <0.2M. K increases with decreasing concn. to a max. of 60°. W. R. A.

Vapour pressure of metals. I. Vapour pressure of magnesium over aluminium-magnesium alloys. II. Vapour pressure of zinc over aluminium-zinc alloys. A. Schneider and E. K. Stoll (*Z. Elektrochem.*, 1941, **47**, 519—526, 527—535).—I. The v.p. of Mg over a series of Al-Mg alloys was determined at 600—850° by the transpiration method using electrolytic H₂ as carrier gas. The results were combined with those of Eucken (A., 1936, 418) to extend the range down to 544°. Heats of vaporisation (λ) were calc. from the Clausius-Clapeyron equation. The partial molar heats of mixing at 719° were obtained from the vals. of $\lambda_{\text{alloy}} - \lambda_{\text{Mg}}$. Also calc. were the Mg-activities in the alloys and the corresponding vals. of $-\Delta G$. The departure from ideal is less at higher temp.

II. The v.p. of Zn over a series of Al-Zn alloys was determined by Hargreaves' method (A., 1939, I, 314), which depends on making the v.p. of Zn over the alloy equal to the v.p. of pure Zn at a lower temp. While the melt remains homogeneous, the graph $\log p-1/T$ is a straight line. Below the liquidus line, a Zn-enriched liquid and a solid solution are obtained, causing an increase in the v.p. of Zn. Below the solidus line, $\log p$ again lies on the straight line. The partial molar heat of mixing is very small and the heat of vaporisation is almost independent of the composition of the alloy. Zn-activities and $-\Delta G$ vals. were calc. for two temp. The results indicate that the system Al-Zn behaves as a mixture. J. F. H.

Constitution of silver-magnesium alloys in the region 0—40 at.-% magnesium. K. W. Andrews and W. Hume-Rothery (*J. Inst. Metals*, 1943, **69**, 485—493).—Thermal analysis and X-ray examination show that the solubility of Mg in Ag rises from 26.5 at.-% at 300° to 29.3 at.-% at the eutectic temp. (759.3°) while the phase is homogeneous at ~40 at.-% Mg at 300° and 35.5 at.-% Mg at 759.3°. The eutectic composition is 33.4 at.-% Mg. Prolonged annealing of alloys with ~25 at.-% Mg appears to produce a superlattice structure. A. R. P.

Constitution of magnesium-manganese-zinc-aluminium alloys in the range 0—5% Mg, 0—2% Mn, and 0—8% Zn. IV. Equilibrium diagram below 400°. A. T. Little, G. V. Raynor, and W. Hume-Rothery (*J. Inst. Metals*, 1943, **69**, 467—484).—The Mg-Zn-Al system from the Al-Zn line up to the Al₂Mg₃Zn₄ (7) point has been examined by thermal, X-ray and micrographic methods at temp. below 400°. The $a/(a+T)$ boundary is of the form $[Mg]/[Zn] = K$ where K varies with the temp. according to the expression

$d \log K/d\theta = Q/R\theta^2$ (θ is abs. temp.). In alloys with >~50% Zn and low Mg ($\alpha + \text{MgZn}_2$) and MgZn_2 fields exist but MgZn_2 is never formed under ordinary annealing conditions in alloys richer in Al. The decomp. of the binary α -Al-Zn solid solution into two face-centred cubic structures of different compositions introduces complications into the ternary system, some of which are described with reference to diagrams. Introduction of Mn into the ternary alloys results in the formation of MnAl₃ which is practically insol. in Mg-Zn-Al alloys below 400°; the equilibria in the quaternary system can therefore be calc. from those in the ternary by deducting the Al combined with Mn and treating the remainder of the alloy as a ternary Mg-Zn-Al alloy. A. R. P.

The iron-nickel phase diagram by magnetic analysis and the effects of cold-work. K. Hoselitz (*Iron and Steel Inst.*, Nov., 1943, *Advance copy*, 13 pp.).—The rate of approach of quenched alloys in the Fe-Ni system towards equilibrium at low temp. appears to be hastened by cold-work. In alloys containing 29—35% of Ni, this treatment causes the original single-phase alloy to separate into two phases which are readily detected by measuring the force exerted on a small specimen in a strong inhomogeneous magnetic field. Inconclusive results, however, were obtained when cold-worked samples were annealed at ~500°. J. C. C.

Ionisation constant of carbonic acid and solubility of carbon dioxide in water and aqueous salt solutions from 0° to 50°.—See A., 1944, I, 37.

Solubility of deuterium in solid nickel. A. Sieverts and W. Danz (*Z. anorg. Chem.*, 1941, **247**, 131—134).—The solubility of D₂ in solid Ni at 200—1120° has been determined. It is somewhat < that of H₂. F. J. G.

Solutions of oxygen in metallic titanium. P. Ehrlich (*Z. anorg. Chem.*, 1941, **247**, 53—64).—Ti forms solid solutions with O up to the composition TiO_{0.42}. With increasing O content, a increases to 2.96 Å. at TiO_{0.2} and then remains const., whereas c increases continuously to 1.623 Å., so that c/a approaches the ideal val. for hexagonal close-packing. At the same time ρ increases to 4.92 at TiO_{0.4}. The O atoms occupy the octahedral spaces in the Ti lattice. There is a max. of v.p. at TiO_{0.2}. F. J. G.

Solubilities of normal aliphatic amides, anilides, and *NN*-diphenylamides. A. W. Ralston, C. W. Hoerr, and W. O. Pool (*J. Org. Chem.*, 1943, **8**, 473—488).—The solubilities of octo-, deco-, laur-, myrist-, palmit-, and stear-amide, and of the anilides and *NN*-diphenylamides of decoic, lauric, palmitic, and stearic acid have been determined in C₆H₆, cyclohexane (I), CCl₄, EtOAc, BuOAc, COMe₂, COMeEt, MeOH, 95% EtOH, Pr²OH, Bu²OH, EtNO₂, and MeCN. Unstable modifications of deco- and laur-anilide have been observed. The absence of a homologous influence in the amide series is striking since there appears to be no orderly arrangement of the solubility graphs of these compounds in the less polar solvents. In the three highly polar solvents, EtNO₂, MeOH, and MeCN, the solubilities decrease with increasing mol. wt. although the intervals between the curves are not regular. All the *N*-substituted derivatives appear in orderly sequence in all solvents. The solubility curves for the *NN*-diphenylamides in C₆H₆ are characteristic of compounds which are associated in solution, in that the concn. is practically a linear function of the temp. The amides and anilides exhibit the marked deviation from linearity which is typical of the solubility curves of long-chained compounds which are associated in solution. Only in C₆H₆ are the solubilities of all the *NN*-diphenylamides linear with temp.; in all other solvents the curves of the higher members deviate from linearity and in the most polar solvents even the lower members of the series give irregular solubility curves. The general correlation appears between the solubilities of the amides and the polarities of the solvents. Generally, the solubilities of a given compound at a given temp. are relatively the same in non-polar solvents as in the most polar solvents investigated whilst the solubilities are relatively much greater in the solvents of intermediate polarity, being greatest in the alcohols. Even in solvents of the same polarity, e.g. C₆H₆ and (I), there is at 70° for instance as much as 25- to 50-fold difference in the solubilities of a given amide. In general, the substituted amides behave similarly to the amides with respect to the polarities of the solvents except that the solubilities of the *NN*-diphenylamides decrease markedly with increased polarity of the solvent. None of the structures yet proposed for the amides and their derivatives can adequately explain the anomalous behaviour of these compounds. All the proposed theories imply a semblance of homology. The assumption of polyamide formation does not in itself explain the anomalous solubilities of octo- and myrist-amide. The fact that the Ph substituent of the anilides precludes the formation of polyamides larger than dimerides by H-bonding does not explain why the slopes of the anilide solubility curves are less steep and break more sharply in dil. solutions than do those of the corresponding amides. There is no present explanation of the deviation from linearity of the solubility curves of the *NN*-diphenylamides if it is assumed that *NN*-disubstitution prevents association by H-bonding. H. W.

Solubility of salts and salt mixtures in water at temperatures above 100°. III. A. Benrath (*Z. anorg. Chem.*, 1941, 247, 147—160).—Solubility data at high temp. are recorded for MnCl_2 , SrCl_2 , SrBr_2 , BaBr_2 , CdCl_2 , and CdBr_2 . Transition points are indicated as follows: $\text{MnCl}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{MnCl}_2 \cdot \text{H}_2\text{O}$, 198°; $\text{MnCl}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{MnCl}_2$, 362°; $\text{SrCl}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{SrCl}_2 \cdot \text{H}_2\text{O}$, 230°; $\text{SrCl}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{SrCl}_2$, 320°; $\text{SrBr}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{SrBr}_2 \cdot \text{H}_2\text{O}$, 88–62°; $\text{SrBr}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{SrBr}_2$, 345°; $\text{BaBr}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{BaBr}_2$, 350°; $\text{CdCl}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{CdCl}_2$, 174°; $\text{CdBr}_2 \cdot 4\text{H}_2\text{O} \rightleftharpoons \text{CdBr}_2$, 36°. Fused MnCl_2 , SrCl_2 , SrBr_2 , and BaBr_2 are completely miscible with H_2O . F. J. G.

Solubility of gold and silver in thiocarbamide. I. N. Plaksin and M. A. Koshuchova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 671—674).—The influence of acids, alkalis, and oxidising agents on the rate of dissolution of Au and Ag in aq. $\text{CS}(\text{NH}_2)_2$ has been investigated. Deposition of S on the metal is retarded by the addition of FeCl_3 , which also accelerates the dissolution of the metal. Ag is dissolved more quickly than Au. W. R. A.

Diffusion of gases into solids: iron oxide and iron oxide-alumina. G. Graue and H. W. Koch (*Ber.*, 1940, 73, [B], 984—995).—The no. and/or openness of the capillaries in Fe_2O_3 is measured by incorporating during its prep. a trace of ThO_2 , carrying off the emitted emanation in a stream of very pure N_2 , and measuring the α -activity in an electroscope (cf. Hahn, A., 1929, 737). $\text{Fe}(\text{OH})_3$ is prepared by pptn. from the nitrate by NH_3 at 20°, washed, and dried by $\text{EtOH-Et}_2\text{O}$; 10% of $\text{Al}(\text{OH})_3$ may be incorporated; the products are radiographically amorphous. Subsequent heating decreases the rate of evolution of emanation from $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ (10% of Al_2O_3 in this and other cases); from $\sim 500^\circ$ to $\sim 600^\circ$ the decrease is very rapid; from $\sim 600^\circ$ to $\sim 850^\circ$ it is approx. const.; thereafter a rapid rise occurs. The decrease is due to orientation of the mols. occurring with consequent sealing off of the capillaries. With Fe_2O_3 the changes occur $\sim 100^\circ$ earlier (cf. Gottc, A., 1938, I, 412), showing that Al_2O_3 stabilises the condition of disorientation. When d of powders is determined by immersion in a liquid, e.g., xylene, the capillaries remain filled with air; if a powder is introduced into a pycnometer filled with air containing emanation, the capillaries are filled with radioactive air and measurement of the activity of the air in the pycnometer gives the displacement and thus another val. for d . Differences between the two vals. of d indicate the vol. of the capillaries. d of $\text{Fe}(\text{OH})_3$ at 20° is 2.3; heating at 250—1000° gradually increases d to 5.1, the xylene method giving regularly a lower val. Long heating at 450° gives an oxide which has $d \sim 5.1$ at 150—510°. Similar measurements for $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ show rather longer persistence of the fine pores. When Fe_2O_3 or $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ containing emanation, heated to const. d at 450°, is heated, the rate of evolution of emanation remains const. to $\sim 620^\circ$ and $\sim 820^\circ$, respectively, thereafter rising very rapidly; this rise is due to movement of mols. temporarily uniting holes in the solid; the Al_2O_3 has the same effect as in other measurements. Hahn's capsule method (A., 1935, 32) shows a similar effect. Diffusion of gas into Fe_2O_3 , determined by emanation, rises rapidly from $\sim 620^\circ$; this change occurs at higher temp. for $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$. Adsorption on Fe_2O_3 falls rapidly from 20° to $\sim 150^\circ$, becoming thereafter nearly const. Fe_2O_3 and $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ give identical X-ray spectra, indicating that the Al_2O_3 "dissolves" in the Fe_2O_3 lattice. R. S. C.

Electrification and luminescence phenomena accompanying desorption of gases from metals. J. W. McBain and C. I. Glassbrook (*J. Amer. Chem. Soc.*, 1943, 65, 1908—1909).—When H_2 , O_2 , air, natural gas, or H_2O , MeOH , or CCl_4 vapours are passed over cooling Pt or Ni, previously heated to 1000—1500° in a vac., the escaping gases become electrified and can cause luminescence on the walls of a SiO_2 tube. The effect is ascribed to electrified ultramicroscopic particles ejected from the metal by sorption and desorption, the luminescence being due to the gaseous ionisation they produce. W. R. A.

Sorption and surface area in silica aerogel. S. S. Kistler, E. A. Fischer and I. R. Freeman (*J. Amer. Chem. Soc.*, 1943, 65, 1909—1919).—Sorption of vapours of H_2O , CCl_4 , SiCl_4 , and C_6H_6 on SiO_2 aero- and xero-gels has been determined at various temp. The area under the wt. adsorbed-log (p_0/p) curve (p = partial v.p., p_0 = saturation v.p.) is a measure of the total surface area of the gel. Capillary condensation, for non-aq. liquids on SiO_2 gel, may account for nearly all the measured adsorption. Removal of H_2O from the gel does not alter the form of the adsorption curve. W. R. A.

Absorption of nitrous gases by silica [and alumina] gel and by calcium and beryllium hydroxides. E. Briner and E. Lowy (*Helv. Chim. Acta*, 1943, 26, 1054—1064).— $\text{Al}(\text{OH})_3$ gel is rather less effective than SiO_2 gel for the reversible absorption of dil. nitrous gases. $\text{Be}(\text{OH})_2$ has a slight but definite effectiveness, $\text{Ca}(\text{OH})_2$ none. F. J. G.

Influence of sorption on electrical conductivity of pulverised sorbents.—See A., 1944, I, 39.

Gibbs' formula and so-called negative adsorption. J. Palacios and R. Salcedo (*Anal. fis. quim.*, 1943, 39, 215—218).—An approx. expression $\gamma - \gamma_0 = ATc$ is deduced for dil. solutions (γ and γ_0 are

the surface tensions of the solution and solvent, A is a const., and c the concn.). F. R. G.

Surface tension of Wisconsin Lake waters. Y. Hardman (*Trans. Wisconsin Acad. Sci.*, 1941, 33, 395—404).—When a film of organisms is present a depression of the surface tension of the H_2O is found. L. G. G. W.

Potential, impedance, and rectification in membranes. D. E. Goldman (*J. Gen. Physiol.*, 1943, 27, 37—60).—Membranes of collodion, collodion-lecithin, collodion-kephalin, onion cuticle, and proteins behave as parallel resistance-capacity combinations when separating solutions of electrolytes. The capacities of the above membranes vary slightly with the concn. and nature of the solutions and have phase angles 88—89°, 79—82°, 84—86°, 83—85°, 65—75°, respectively. The conductances A are approx. \propto those of the solutions but are much smaller and, like the dielectric consts., are $>$ those of the membrane material in bulk. In general A varies with current but the capacity is independent of current. Approx. vals. for the membrane potentials V indicate a linear proportionality with the log of the ratio of the concns. of electrolyte on both sides of the membrane. The amount of rectification produced by the membranes increases with V rather than with the concn. ratio of A . By considering the presence of fixed as well as mobile ions, the Planck derivation of liquid junction potential is extended to membranes, and expressions are obtained for V and for the variation of A with current. The calc. vals. show qual. agreement with experiment. J. H. B.

Study of "disjoining action" under conditions of sorption of water vapour. M. V. Tschapek (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 588—590).—The "disjoining action" is the process by which mutual contact of dispersed particles is prevented by the dispersion medium. The swelling of cylinders prepared from dispersed quartz sand and kaolin, when exposed to H_2O vapour, was determined. Even in the vapour phase, the dispersed particles come in contact through the sorbed vapour. The disjoining action takes place at v.p. at which capillary condensation is improbable. A. J. M.

Unrolling of fibre molecules in flowing solutions. W. Kuhn and H. Kuhn (*Helv. Chim. Acta*, 1943, 26, 1394—1465).—In flowing liquids fibre-type mols. of high polymerides tend to unroll and become elongated in the direction of flow. The effects of this behaviour on the physical properties of the solution are discussed mathematically and relationships are developed expressing the streaming double refraction and viscosities of such solutions in terms of the degree of polymerisation. J. W. S.

Charge and stability of colloids. II. Effect of non-electrolytes. H. P. Yadava (*J. Indian Chem. Soc.*, 1943, 20, 110—114).—Addition of MeOH lowers slightly the adsorption of Ba^{++} and SO_4^{--} ions on As_2S_3 and $\text{Fe}(\text{OH})_3$ sols, respectively. EtOH in low concn. causes an increased adsorption but this effect decreases at higher $[\text{EtOH}]$. Agar-agar and gelatin in low concns. cause a slight increase in adsorption but higher concns. cause a slight decrease. MeOH causes sensitisation towards pptn., whereas the other materials have a stabilising effect. This is explained as due to complex formation between the MeOH and the sol. J. W. S.

Opacity changes in gel-forming mixtures during setting. II. Thorium phosphate, cerium phosphate, thorium arsenate, and stannic phosphate gels. T. V. Desai and S. Guruswamy (*Proc. Indian Acad. Sci.*, 1943, 18, A, 31—39; cf. Prasad and Gogate, A., 1943, I, 256).—Th and Ce phosphate gels give an exponential opacity-time relation. The rate of change of opacity is increased by HCl and decreased by non-electrolytes. Final opacity vals. depend on the concn. of the constituents of the gel-forming mixture. L. J. J.

Structure development in rubber sols under the action of active fillers. P. Rebinder, G. A. Ab, and S. J. Veiler (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 444—447).—In presence of active SiO_2 sols of Na-butadiene rubber (10—11% in PhMe) develop a continuous structure. Even with $[\text{SiO}_2] = 0.76\%$ there is an appreciable increase in yield val. and anomalous η . Inactive fillers (ground CaCO_3 , marshallite, orthoclase) have no structure-forming properties. It is possible that besides transferring the rubber into the film-like state of solvate films, active filler particles act as centres for continuous structure formation by orienting polymer chains under the action of the adsorption field of the particles. Presence of H_2O in the SiO_2 inhibits structure formation. Structure formation also occurs in sols prepared in light petroleum and CHCl_3 . C. R. H.

Fine structure of cellulose fibres. H. Staudinger (*Z. Elektrochem.*, 1941, 47, 637—638).—A reply to Meyer (A., 1943, I, 300). F. J. G.

Osmotic pressure and viscosity measurements with cellulose acetate fractions. A. Bartovics and H. Mark (*J. Amer. Chem. Soc.*, 1943, 65, 1901—1905).— η_{sp} . (<0.5 vol.-%) and π (<0.8 wt.-%) of cellulose acetate fractions in COMe_2 and $\text{COMe}_2\text{-MeOH}$ have been determined. The equations of Flory (A., 1942, I, 364) and Huggins (A., 1939, I, 318; 1943, I, 58) were applicable to all fractions, with $h' = 0.70$ and $\mu = 0.43$ in COMe_2 , and 0.60 and 0.46 in $\text{COMe}_2\text{-MeOH}$.

In the equation $[\eta] = KM^a$ (M — mol. wt., $[\eta] = \eta_{sp}$ at zero concn., K and a const.), $K = 1.04 \times 10^{-2}$, $a = 0.67$. W. R. A.

VI.—KINETIC THEORY. THERMODYNAMICS.

Calculation of chemical equilibria and its recent progress. C. G. Boissonnas (*Helv. Chim. Acta*, 1943, 26, 1383—1393).—The calculation of the equilibrium const. of a reaction at any temp. and of the entropy of a perfect gas is discussed. J. W. S.

Statistical mechanics of dimerisation in perfect solutions. G. S. Rushbrook (*Proc. Camb. Phil. Soc.*, 1943, 39, 202—204).—The Gibbs free energy is calc. statistically for a liquid or solid binary solution in which dimerisation may occur in the solute. H. J. W.

Silver thiosulphate complexes in aqueous solution. O. Schmitz-Dumont and E. Schmitz (*Z. anorg. Chem.*, 1941, 247, 35—52).—Measurements on concn. cells indicate that solutions of $\text{Ag}_2\text{S}_2\text{O}_3$ in $2M\text{-Na}_2\text{S}_2\text{O}_3$ contain the complex ion $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{2-}$. F. J. G.

Ionisation of strong electrolytes. I. General. Nitric acid. O. Redlich and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1943, 65, 1883—1887).—The intensities of Raman lines of HNO_3 solutions have been determined. Comparison of the data with those for NaNO_3 solutions establishes the complete ionisation of HNO_3 ; thermodynamic ionisation const. 21. A characteristic Raman spectrum is considered a sufficient criterion of the existence of undissociated mols. in solution. W. R. A.

Dissociation constants of monobasic acids. II. Extrapolation method. III. Strengths of some cyano-acids. D. J. G. Ives and K. Sames (*J.C.S.*, 1943, 511—513, 513—515).—II. Ives' extrapolation method (A., 1933, 780) applies accurately to conductivity measurements free from systematic errors, and is of val. in the determination of all consts. The use of BzOH as standard electrolyte is recommended.

III. Vals. of $K \times 10^5$ for cyanoacetic, β -cyanopropionic, γ -cyano-*n*-butyric, cyclohexyl- and dimethyl-cyanoacetic, and *trans*-1-cyanocyclohexane-2-carboxylic acids, measured by a conductivity method with the authors' extrapolation equation, are 342, 10.2, 3.66, 430, 380, and 13.65, respectively. The effect of $\cdot\text{CN}$ as substituent is \gg that of the halogens, which is shown to be mainly electrostatic. The enhanced effect with $\cdot\text{CN}$ is due to its polarisability. K may be related with the dipole moment of the substituent, provided that the effect is purely inductive, and that free rotation of bonds does not interfere. L. J. J.

Ionisation constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions from 0° to 50° . H. S. Harned and R. Davis, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 2030—2037).—The solubility of CO_2 in H_2O and aq. NaCl at 0 — 50° has been determined by analysing the solutions used in cells of the type $\text{Pt-H}_2, \text{CO}_2|\text{NaHCO}_3 (m_1), \text{NaCl} (m_2), \text{CO}_2 (m_3)|\text{AgCl-Ag}$. Logarithms of the Henry's law consts., computed from these determinations, are expressed by quadratic equations. K of H_2CO_3 at 5° intervals from 0° to 50° has been calc. from the e.m.f. data, and $\log K$ expressed as a function of T . Vals. of ΔG° , ΔH° , ΔC_p° , and ΔS° have been calc. W. R. A.

Activity coefficients of lead chloride determined from e.m.f. and solubility data at 25° in ethylene glycol-water solutions. A. B. Garrett, R. Bryant, and G. F. Kiefer (*J. Amer. Chem. Soc.*, 1943, 65, 1905—1907).—The solubility of PbCl_2 has been determined in $(\text{CH}_2\text{OH})_2\text{-H}_2\text{O}$ solutions (0, 20, 40, 60, and 80 wt.-% H_2O) containing KCl . The e.m.f. of the cell $\text{Pb(Hg)}|\text{PbCl}_2, \text{AgCl}|\text{Ag}$ in these solutions has been determined. Activity coeffs. of PbCl_2 solutions have been calc. W. R. A.

Niobium and hydrogen, niobium and deuterium. A. Sieverts and H. Moritz (*Z. anorg. Chem.*, 1941, 247, 124—130).—Isotherms and isobars for the systems Ni-H and Ni-D are recorded. They agree within the experimental error. F. J. G.

X-Ray studies on the system cadmium bromide-cadmium iodide.—See A., 1943, I, 300.

X-Ray investigation of the systems $\text{CaO-Bi}_2\text{O}_3$, $\text{SeO-Bi}_2\text{O}_3$, and $\text{BaO-Bi}_2\text{O}_3$ -O. (Mixed oxides with a defect oxygen lattice.) B. Aurivillius (*Arkiv Kemi, Min., Geol.*, 1943, 16, A, No. 17, 13 pp.). When the Ca (Sr, Ba) fraction ($= \text{Ca/Ca} + \text{Bi}$) is gradually increased, the first phase to appear, after $\alpha\text{-Bi}_2\text{O}_3$, is rhombohedral. The cell dimensions and metal parameters for each system are given. In the $\text{CaO-Bi}_2\text{O}_3$ system, this rhombohedral phase is followed by a phase of const. composition. In $\text{SrO-Bi}_2\text{O}_3$ several other phases appear. In $\text{BaO-Bi}_2\text{O}_3$, when the Ba fraction is increased, one, or possibly two, tetragonal phases of variable composition are formed. A. J. M.

Active substances. XLVIII. Effect of the physical state of the solid reactants on the equilibrium $\text{Fe/Fe}_3\text{O}_4$ with $\text{H}_2\text{O/H}_2$. R. Fricke, K. Walter, and W. Lohrer (*Z. Elektrochem.*, 1941, 47, 487—500).—The equilibrium $3\text{Fe} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2$ was studied between 360° and 550° by keeping a const. steam pressure and

measuring the partial pressure of H_2 . Two forms of Fe were used: "active" Fe prepared by reduction of hydrated Fe_2O_3 at a temp. just $>$ temp. of measurement, and "inactive" Fe prepared by reduction at 685° . The equilibrium was approached from both sides, but in several cases the two results obtained were not concordant. The heat of reaction (W_p) using active Fe is $>$ that using inactive Fe. X-Ray investigation showed that active Fe had a smaller particle size than inactive Fe. The results were not sufficient to account for the large differences in W_p , but this may be due to the fact that X-ray vals. are always average vals., whereas only the more active particles participate in equilibria. The solubility of H_2 in Fe affects W_p by only a few tenths kg.-cal. J. F. H.

Fusion diagram for the system LiF-KF-NaF . A. G. Bergman and E. P. Dergunov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 753—754).—The equilibrium diagram is given. In the binary system KF-NaF , the eutectic is at 710° and 40 mol.-% NaF . In the system LiF-NaF , the eutectic temp. is 652° (39 mol.-% NaF), and in the system LiF-KF it is 492° (50 mol.-% KF). For the ternary system the eutectic temp. is 454° (11.5 mol.-% NaF , 42 mol.-% KF). The very considerable lowering of m.p. of the individual constituents is noticeable. A. J. M.

Fusion diagram of the system LiF-NaF-MgF_2 . A. G. Bergman and E. P. Dergunov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 755—756).— LiF and MgF_2 form a continuous series of solid solutions with a min. at 742° (33 mol.-% MgF_2). In the binary system NaF-MgF_2 , a compound NaF.MgF_2 , m.p. 1030° , is formed. It forms a eutectic with NaF (75 mol.-% NaF) at 830° , and with MgF_2 (64 mol.-% MgF_2) at 1000° . There are two ternary eutectic points. In the system LiF-NaF-NaF.MgF_2 , the eutectic separates at 630° (10 mol.-% MgF_2 , 43 mol.-% NaF , 47 mol.-% LiF). In the system $\text{LiF-MgF}_2\text{-NaF.MgF}_2$, the eutectic separates at 684° (29 mol.-% MgF_2 , 12 mol.-% NaF , 59 mol.-% LiF). A. J. M.

Merwinite (3CaO.MgO.2SiO_2) and its stability relations within the system CaO-MgO-SiO_2 (preliminary report). E. F. Osborn (*J. Amer. Ceram. Soc.*, 1943, 26, 321—332).—Investigations on compositions between 2CaO.SiO_2 and 2CaO.MgO.2SiO_2 (I), between 3CaO.MgO.2SiO_2 (II) and (I), and between (II) and CaO.MgO.SiO_2 , indicate that a field of (II) appears on the liquidus surface of CaO-MgO-SiO_2 , and that (II) melts incongruently at 1575° to 2CaO.SiO_2 , MgO , and liquid. Extensive new and correcting data are recorded for various invariant points and joins. J. A. S.

Thermochemistry of alloys. VIII. Heats of fusion of alloys and entropy change on fusion in relation to the degree of orientation. Heats of mixing of several liquid alloys. O. Kubaschewski (*Z. Elektrochem.*, 1941, 47, 476—484).—From measurements of the heat content between room temp. and temp. $>$ m.p. the heats of fusion (L) of the alloys CdSb , Ti_3Pb_3 , Ti , Pb , Bi_2Ti_2 , Bi_2Ti_1 , Cu_2Cd_3 , and Mg_2Pb were determined. The vals. of L for Hg_2Ti_2 and Mg_2Sn were obtained by different methods. From the results the entropy changes at fusion (ΔS_{exp}) were determined and compared with the calc. vals. (ΔS_{add}) obtained by compounding additively the ΔS vals. of the pure components. The value $\Delta S_{\text{exp}} - \Delta S_{\text{add}}$ gives an indication of the degree of orientation of the alloy, being 0 for an unoriented alloy and > 0 for an oriented alloy. It is shown that CdSb , Mg_2Pb , and Mg_2Sn are completely oriented, the last two having a fluorspar type lattice. Cu_2Cd_3 , Cu_2Cd_2 , and Ti_3Pb_3 are partly oriented; the other alloys are unoriented. The treatment was also applied to some measurements by Roos (A., 1916, ii, 293). The heats of mixing of the following alloys were determined: CdSb 900 g.-cal. per g.-atom at 650° , Cu_2Cd_3 90 g.-cal. per g.-atom at 600° , Bi_2Ti_1 1110 g.-cal. per g.-atom at 400° , Bi_2Ti_1 850 g.-cal. per g.-atom at 400° . J. F. H.

Thermochemistry of alloys. IX. Heats of formation of some alloys and the connexion between heat evolution and contraction on alloy formation. O. Kubaschewski (*Z. Elektrochem.*, 1941, 47, 623—630).—Heats of formation are recorded as follows: LiTi , 6.4; NaTi , 4.5; NaTe , 20; NaTe , 15; NaTe , 7.5; ZnTe 14.7 kg.-cal. per g.-atom. In general, in any given structure type there is a parallelism between heat of formation and contraction, which is modified when the co-ordination no. of one of the constituents is different in the free state. F. J. G.

Transition temperatures and heats of transition of the alkali hydrosulphides and hydroselenides. W. Teichert (*Z. anorg. Chem.*, 1941, 247, 113—123).—The heat contents of NaSH , KSH , RbSH , NaSeH , KSeH , and RbSeH from room temp. to temp. $\sim 30^\circ >$ the transition temp. are recorded. The transition temp. are: NaSH , 85° ; KSH , 180° ; RbSH , 130° ; NaSeH , 86° ; KSeH , 176° ; RbSeH , 147° ; and the heats of transition: NaSH , 0.7; KSH , 0.55; RbSH , 0.4; NaSeH , 0.7; KSeH , 0.45; RbSeH , 0.25 kg.-cal. per g.-mol. F. J. G.

Heat of dissolution of ethane and propane. R. A. Budenholzer, B. H. Sage, and W. N. Lacey (*Ind. Eng. Chem.*, 1943, 35, 1214—1220).—The enthalpy changes involved in the dissolution of C_2H_6 and $n\text{-C}_3\text{H}_8$ in a non-volatile, paraffin-base, H_2O -white oil have been determined with an accuracy of 1.5%. Measurements of the influence of temp. on sp. vol. and pressure at bubble point of mix-

tures of C_3H_8 and oil have also been made. Smoothed vals. of enthalpy change at even compositions at 37.8° and 71.1° and additionally at 104.4° for C_3H_8 are tabulated. Comparison is made between vals. obtained by calorimetric determinations and those calc. from the vol. behaviour of the system. C. R. H.

Volume of mixing and thermodynamic functions of benzene-carbon tetrachloride mixtures. S. E. Wood and J. P. Brusie (*J. Amer. Chem. Soc.*, 1943, **65**, 1891—1895).—The increase in vol. on mixing CCl_4 and C_6H_6 has been measured at 15—75° and at const. pressure. Vals. of ΔG , ΔH , and ΔS of mixing have been calc., and vals. of ΔA and ΔE derived from the data for 25°, 40°, and 70°. Vol. of mixing increases ~9-fold; excess S of mixing at const. vol. decreases by ~50% from 25° to 70°. W. R. A.

Free energy of methyl ether from the methanol-methyl ether equilibrium $2MeOH(v.) = Me_2O + H_2O(v.)$. P. H. Given (*J.C.S.*, 1943, 589).—Recalculation of $\Delta G_{298.1}^\circ$ from recent published thermodynamic data gives -28,500 g.-cal. L. J. J.

VII.—ELECTROCHEMISTRY.

Antimony-caesium films. P. G. Borziak (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 546—549).—Investigation of the sign of the thermo-e.m.f. of Sb-Cs films in different stages of formation indicates that they have predominantly a hole conductivity, which, however, becomes electronic on introduction of excess of Cs into the film. If excess of Cs is added to a formed film, its dark conductivity decreases, but rises again on removal of the excess of Cs. The photo-conductivity of the films is discussed. A. J. M.

Superconductivity of tin-zinc eutectics. E. L. Andronikashvili (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 541—542).—Molten Sn-Zn alloys were solidified at liquid air temp. and were then annealed at a temp. near the eutectic. Up to 1.5° K., the magnetic moment of the alloy is practically independent of [Sn], and is equal to the magnetic moment of Sn of equal vol. The threshold temp. at which superconductivity sets in is the crit. temp. of Sn (3.69° K.). Curves of magnetic moment against magnetic field show the "tails" characteristic of the disperse state. When the superconductivity of the alloys is destroyed, there is an appreciable time lag, in contrast with the effect in pure Sn. The results may be explained by supposing that the Sn screens the Zn grains. This effect may possibly be eliminated by suitable heat-treatment. A. J. M.

Conductometric study of the acids H_2RO_3 . R. Duckert, P. Kohler, and P. Wenger (*Helv. Chim. Acta*, 1943, **26**, 1166—1172).—A for mixtures of $Al(OH)_3$ gel with lactic or pyruvic acid decreases markedly with time, especially with lower concns. of org. acid. This behaviour is attributed to the formation of complex acids. F. J. G.

Influence of sorption on electrical conductivity of pulverised sorbents. N. A. Figurovski and M. M. Feinberg (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 344—346).—The electrical conductivity of pulverised charcoals deposited from suspensions on to pumice, ebonite, porcelain, and other dielectrics was determined after the deposits had adsorbed C_6H_6 , PhMe, aliphatic alcohols, Et_2O , CCl_4 , and other substances from their mixture with air. There is a decrease of resistance with time of sorption up to a limit, which, in the case of the alcohols, is the greater the higher is the mol. wt. of the alcohol. The nature of the sorbed substance influences the rate and final val. of the resistance decrease. The speed with which equilibrium is reached shows that the reversible sorption takes place mainly on the surface and in the macropores of the charcoal. A. J. M.

Cu/Cu⁺ potential in concentrated copper sulphate solutions at different temperatures. I. F. Müller and H. Reuther (*Z. Elektrochem.*, 1941, **47**, 640—644).—E.m.f. data for the cells $Cu \text{ amalgam} | CuSO_4(a), Hg_2SO_4 \text{ (saturated)} | Hg$ are recorded for conc. $CuSO_4$ solutions (up to saturation) at 11.5—50°. The normal potential $Cu(Hg) | Cu^+$ is = 0.3454 v. F. J. G.

Variations of the potentials of the ozone and oxygen electrodes under the influence of ultra-violet radiation. E. Briner and A. Yalda (*Helv. Chim. Acta*, 1943, **26**, 1368—1370).—Exposure to ultra-violet radiation decreases the potential of an ozonised- O_2 (2% O_3) on Pt electrode in both 38% and 0.1N- H_2SO_4 ; the effects with polished and platinised electrodes are approx. equal. The potential of an O_2 -Pt electrode, however, is increased, the effect with polished being > with platinised Pt, but the potential is still < the theoretical val. for a reversible O_2 electrode. These results are in accord with the observations that O_3 is decomposed, and O_2 slightly ozonised, in ultra-violet light and that O_3 is decomposed on platinised Pt. J. W. S.

Cause of the asymmetric potential of glass electrodes. W. Brauer (*Z. Elektrochem.*, 1941, **47**, 638—639).—The dependence of the asymmetric potential of glass electrodes on the history of the two surfaces indicates that differences in their alkali content, and not mechanical strains, are the cause of this potential. F. J. G.

Influence of non-electrolytes on the decomposition potential of aqueous silver nitrate. D. N. Solanki (*J. Indian Chem. Soc.*, 1943, **20**, 105—109).—The decomp. potential of 0.1N- $AgNO_3$ at 30° is unaltered by the presence of 0—50 vol.-% of $EtOH$, glycerol, or C_6H_5N , although the sp. resistance of the solution increases with increasing concn. of non-electrolyte. The decomp. potential, however, is raised from 0.75 to 0.85 v. in the presence of 5 vol.-% of $COMe_2$, but is unaltered at higher concn. This is attributed to the formation of a stable complex of $AgNO_3$ with $COMe_2$. J. W. S.

Oxidation potentials of methoxyacetophenones. R. H. Baker and J. G. Schafer (*J. Amer. Chem. Soc.*, 1943, **65**, 1675—1676).—By equilibration with fluorenone in $NMe_2 \cdot OH-Pr^tOH$, $COPhMe$ and its *o*-, *m*-, and *p*- OMe -derivatives are shown to have E_0 151, 160, 158, and 129 mv., and $-\Delta F$ 7.0, 7.4, 7.3, and 6.0 kg.-cal., respectively. The low val. for the *p*-compound is due to its being a vinologue of an ester; absence of this effect for the *o*-compound is ascribed to intra-mol. H-bonding of the reduced form. R. S. C.

Revision of the oxidation potentials of the *o*-phenanthroline and dipirydil ferrous complex. D. N. Hume and I. M. Kolthoff (*J. Amer. Chem. Soc.*, 1943, **65**, 1895—1897).—The oxidation potential of Fe^{II} -*o*-phenanthroline and -2:2'-dipyridyl in 1M- H_2SO_4 or -HCl is 1.06 v., instead of the reported val. (1.14 v.). W. R. A.

Oxidation potential of the chromocyanide-chromicyanide couple and polarography of the chromium cyanide complexes. D. N. Hume and I. M. Kolthoff (*J. Amer. Chem. Soc.*, 1943, **65**, 1897—1901).—The reaction $Cr(CN)_6^{4-} \rightleftharpoons Cr(CN)_6^{3-} + e$ has been studied polarographically and potentiometrically. It is reversible at the dropping Hg electrode in 1M-KCN, with an oxidation potential of -1.14 v. The standard potential is estimated to be -1.28 v. W. R. A.

Electrical activity of acetylcholine, choline, adrenaline, and benzedrine. R. Bentner and T. C. Barnes (*Biodynamica*, 1942, **4**, 47—55).—Acetylcholine (I) (1 part in 3×10^8) in 0.7% NaCl in contact with triacetin no p.d. develops. To produce the same p.d. a solution of choline in 0.1% NaOBz of 1 part in 10^7 should be needed. Adrenaline gave a negative p.d. which soon decreased in magnitude. Benzedrine gave a similar but smaller and more stable negative p.d. and also gave a p.d. when in contact with triacetin. The negative p.d. produced by (I) at such low concn. may explain its effect on nerve fibres. L. G. G. W.

Part played by overvoltage and ohmic resistance in the passivity of lead. B. N. Kabanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 339—343).—The resistance of a Pb electrode rendered passive by a film of $PbSO_4$ was determined, taking into account the phase displacement of the a.c. used. The ohmic component decreases with frequency and amounts to only 19 ohms in a fully passive electrode. The ohmic resistance plays no part in the potential change on passivation. This change of potential is connected with the c.d. in the pores of the layer. A. J. M.

Crystallisation of lead sulphate and the thickness of the passive layer on lead. B. N. Kabanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 581—584).—The quantity of electricity necessary to render passive a previously reduced Pb electrode in dil. H_2SO_4 has been determined, the effect of c.d., temp., and concn. of the H_2SO_4 , and the presence of org. compounds being investigated. The thickness of the layer required to render the Pb passive decreases, and the supersaturation of the $PbSO_4$ increases, with increasing c.d. The thickness of the layer is 4—6 times as great in aq. H_2SO_4 as in a 40% $EtOH-H_2O-H_2SO_4$ solution containing the same $[H_2SO_4]$. A. J. M.

Chemistry and structure of anodically produced precipitates and films. I. Anodic behaviour of zinc in a bath of sodium hydroxide. K. Huber (*Helv. Chim. Acta*, 1943, **26**, 1037—1054).—According to conditions, Zn anodes in NaOH become coated with a loose coating of γ -Zn(OH) $_2$ together with a little ZnO (active anodes) or a dark coherent coating having a characteristic structure and oxidising properties (passive anodes). F. J. G.

VIII.—REACTIONS.

Max Bodenstein and chemical kinetics. H. J. Schumacher (*Z. Elektrochem.*, 1941, **47**, 469—475).—An appreciation. J. F. H.

Explosive oxidation of sulphur monoxide. H. Kondratyeva and V. Kondratyev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 128).—Measurements, at 3—13 mm. pressure, of the oxidation velocity determined by the rate of disappearance of the absorption spectrum as a function of O_2 pressure in the temp. range 54—144° show that the reaction velocity rises rapidly with O_2 pressure and becomes immeasurable at the crit. pressure. The measured crit. pressures p_1 satisfy the equation $p_1 - 0.5c^{21.0/RT}$ mm. Hg. If O_2 is forced in at $p > p_1$ there is a slight blue flash lasting a few sec. Near p_1 an induction period lasting ~2 min. at the lowest temp. was observed. Results show that the oxidation is a chain reaction and that the

chains have few branches; p_1 corresponds to the lower ignition limit. N. M. B.

Exchange between ions in solid salts and their radioactive isotopes in solution. E. Gleditsch and R. Rona (5 *Nordiske Kemikermode*, 1939, 184—186).—The rate of exchange of radioactive Cu⁺ in solution with solid CuSO₄·5H₂O is very rapid and increases with decrease in particle size, with solid CuBr and CuI is slower and decreases as the solid ages, and of radioactive Br⁻ and I⁻ with solid CuBr and CuI very slow. M. H. M. A.

Elimination of chlorine from sodium chloroacetate by salts of weak acids. H. M. Dawson, E. R. Pycck, and G. F. Smith (*J.C.S.*, 1943, 617—520).—The initial velocity coeffs. (k) for the reaction between CH₂Cl·CO₂' and 34 anions, which have been measured at 45°, show that there is a general relation between k and the basic strength of the added anion, k increasing with anionic strength. C. R. H.

Bronsted relation in the hydrolysis of the halogenoacetates and the theory of acids and bases. G. F. Smith (*J.C.S.*, 1943, 521—523).—Basic catalysis of the hydrolysis of CH₂X·CO₂' (X = halogen) exhibits the characteristics usually associated with general acid-base catalysis, and the data for CH₂Cl·CO₂' (see preceding abstract) and CH₂Br·CO₂' conform to the Bronsted catalysis relation with certain exceptions, notably the anions OH⁻, SO₃'', and S₂O₃''. Discussion of the theory of acids and bases leads to the view that, contrary to the Lowry-Bronsted definition, the transfer of a proton is not an essential process in basic or acid catalysis. C. R. H.

Kinetics of oxidation of organic compounds by potassium permanganate. VI. Benzaldehyde. F. C. Tompkins (*Trans. Faraday Soc.*, 1943, 39, 280—287).—The reaction in neutral solution is of the second order, with $k = 0.34$ l./g.-mol./sec. at 30–30°, and an activation energy of 11,800 g.-cal. in the range 26.7—45.6°. In alkaline solution k decreases with time, but the extrapolated vals. (k_0) for $t = 0$ increase linearly with [OH⁻] up to 0.15N., when acceleration occurs owing to formation of MnO₄''. In acid solution k increases with time and k_0 is related to [H⁺] by log $k_0 = 1.18 \log [H^+] + 2.26$. Mechanisms similar to those proposed for the oxidation of formate (cf. A., 1941, I, 271) are applicable and the previous theory is confirmed. F. L. U.

Kinetics of the decomposition of trinitrobenzoic acid in dioxan-water mixtures. D. Trivich and F. H. Verhock (*J. Amer. Chem. Soc.*, 1943, 65, 1919—1924).—The kinetics of the decarboxylation of 2:4:6:1-(NO₂)₃C₆H₂·CO₂H have been studied at 10% intervals from 0–90% aq. dioxan, at 60° and 70°, and 0–30%, 80–90% at 80°. The order of reaction varies continuously from 1 at low dioxan concn. to 0.5 at high dioxan concn. The rate has a max. at 80% dioxan. E of activation decreases from 36 kg.-cal. in H₂O to 22 kg.-cal. in 90% dioxan. The variation in order of reaction and the max. in rate are due to the decomp. of the trinitrobenzoate ion; measurements of K give quant. support to this explanation. Variation of E of activation has been related to varying degrees of solvation of the trinitrobenzoate ion. W. R. A.

Kinetics of oxidation of cellulose with periodic acid. G. Goldfinger, H. Mark, and S. Siggia (*Ind. Eng. Chem.*, 1943, 35, 1083—1086).—Curves relating O₂ consumption and time in the oxidation by NaIO₄ at pH < 1 (H₂SO₄) of Hercules Powder cotton linters and cellulose (I) regenerated from Cu(NH₃)₄' can be interpreted as the superposition of a fast and a slow oxidation reaction. The saturation val. for the former corresponds with the total amount of easily accessible (*i.e.*, amorphous) areas of the (I), and can be obtained by extrapolating the linear portion of the curve to the ordinate; it amounts to ~2 wt.-% of the (I). The remainder corresponds with the more difficultly accessible (*i.e.*, cryst.) parts of (I). The method enables the relative amounts of the two phases to be estimated. The ·CHO val. reaches a max. after 16 hr. and falls to ~0 after 24 hr.; the ·CO₂H val. increases most rapidly at the max., and then follows the O₂ curve closely. The oxidation of the individual glucose units is a two-step reaction following approx. a simple kinetic scheme. J. G.

Hydrogen fluoride [as] catalyst. I. Physical and chemical properties. II. Role in organic chemistry. J. H. Simons (*Petrol. Refiner*, 1943, 22, 155—161, 189—193). R. B. C.

Initiation of polymerisation by free radicals. G. V. Schulz (*Z. Elektrochem.*, 1941, 47, 618—619).—Polymerisation by heat, peroxides, and radicals is a free radical process, whilst there is not enough evidence to decide between free radical and polarisation mechanisms in the case of initiation by inorg. catalysts (cf. A., 1943, I, 280). J. H. Ba.

Catalysis of reactions of the mercurous ion. Equilibrium Fe²⁺—Fe³⁺—Hg²⁺—Hg in aqueous perchlorate solutions. P. A. Herrlin (5 *Nordiske Kemikermode*, 1939, 194—195).—The reaction 2Fe(ClO₄)₂ + Hg₂(ClO₄)₂ ⇌ 2Fe(ClO₄)₃ + 2Hg is very slow in absence of catalysts, but is powerfully catalysed by kieselguhr, graphite, and all types of activated C. k increases with increasing catalyst surface and increasing initial [Fe²⁺], but decreases with

increasing initial [Hg₂'']. The catalysis is probably due to the transition Hg₂' → 2Hg' on the active surface. M. H. M. A.

Induced chlorination of maleic acid. Evidence for chain reaction mechanisms. H. Taube (*J. Amer. Chem. Soc.*, 1943, 65, 1876—1882).—The induced chlorination of maleic acid has been studied kinetically. One-electron reducing agents which react with Cl₂ and Ce^{IV}, are equally effective as inductors, whereas one-electron reducing agents which do not react with Cl₂ and O₂ are inhibitors. These results, and the kinetic data, are explained by a chain mechanism involving at. Cl and an org. radical. Relative reaction rates of at. Cl in m-Cl' at 25° with inhibitors and with maleic acid have been determined. W. R. A.

Oxidation processes. XVI. Autoxidation of ascorbic acid. A. Weissberger, J. E. LuValle, and D. S. Thomas, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 1934—1939).—The rate of the autoxidation of L-ascorbic acid (I) has been determined at pH 4.7—9.2 and at 20°, in presence of Cu²⁺ or with CN⁻ and CNS⁻ ions added to suppress catalysis by metal ions. The uncatalysed reaction is first order with respect to (I). The uncatalysed reaction rate depends on pH, showing that both singly and doubly charged ions of (I) are reacting; the rates with O₂ at 760 mm. are 5 × 10⁻⁵ and 5 and are independent of and α the partial pressure of O₂. The rate of the Cu²⁺-catalysed reaction α [O₂] at pH < 7. W. R. A.

Radioactive exchange and adsorption of methyl bromide with several inorganic bromides. G. B. Kistiakowsky and J. R. Van Wazer (*J. Amer. Chem. Soc.*, 1943, 65, 1829—1834).—Exchange of Br between MeBr and inorg. bromides has been studied using Br*. For AlBr₃, which catalyses reactions of MeBr, the activation energy is 4.6 kg.-cal., but for BaBr₂, a less active catalyst, it is 12 kg.-cal. The rate of exchange with KBr is too slow to detect. The differential heat of adsorption of MeBr on BaBr₂ is ~3 kg.-cal., and, as the adsorption is multimol., the rate-determining step in the MeBr-BaBr₂ exchange must be between the BaBr₂ crystals and the adsorbed MeBr. W. R. A.

Rates and temperature coefficients of the hydroxyl-ion-catalysed aldol condensation of benzaldehyde with methyl ethyl ketone and acetone. J. D. Gettler and L. P. Hammett (*J. Amer. Chem. Soc.*, 1943, 65, 1824—1829).—Acid- and base-catalysed aldolisations of PhCHO with COMeEt and COMe₂ have been studied synthetically and kinetically. Selection of experimental conditions can totally eliminate concurrent and consecutive reactions. The OH⁻-catalysed reaction is first order with respect to [PhCHO] and [COMeEt], and the sp. rate is a linear function of [base]^{1/2}, with pronounced medium effects. Vals. of entropy and energy of activation support the theory of Price and Hammett (A., 1941, I, 474) on the effect of structure on the reactivity of carbonyl compounds. W. R. A.

Some reactions of hydroxylamine and the catalytic oxidation of ammonia. M. Bodenstein (*Z. Elektrochem.*, 1941, 47, 501—518; cf. A., 1943, I, 281).—From a study of the properties of NH₂OH, the following reactions are suggested for the catalytic oxidation of NH₃: (1) primary reaction, NH₃ + O = NH₂OH; (2) formation of NO, NH₂OH + O = HNO₂ + H₂O followed by (2a) HNO₂ + O₂ = HNO₃ and (2b) HNO₂ = NO + O + OH, (3) formation of N₂O, NH₂OH + O = HNO + H₂O followed by 2HNO = H₂O + N₂O. (4) N₂ can be formed in two ways: HNO₂ + NH₃ = 2H₂O + N, and HNO + NH₂OH = 2H₂O + N₂. All these reactions have been experimentally confirmed except (2a) and (2b). J. F. H.

Chemistry and structure of anodically produced precipitates and surface films. II. Anodic behaviour of zinc in mixed solutions of sodium hydroxide and sodium salts. K. Huber (*Helv. Chim. Acta*, 1923, 28, 1253—1281; cf. A., 1944, I, 40).—In NaOH-Na₂SO₄, NaOH-Na₂CO₃, and Na₂CO₃-NaHCO₃ baths, as in NaOH, active and passive states of a Zn anode can be sharply differentiated. In NaOH-Na₂SO₄ solutions Zn(OH)₂ of previously unknown lattice structure is deposited on an active anode, whereas a passive anode is coated with a dark oxide film more yellowish than that formed in NaOH. At lower [NaOH] active areas appear on the otherwise passive anode and in these areas there is formed a white ppt. intermediate in composition between Zn(OH)₂ and ZnSO₄·3Zn(OH)₂. An active anode in NaOH-Na₂CO₃ baths yields little and in pure Na₂CO₃ no ppt., a passive anode becoming dark, except with higher bath voltages when the anode in Na₂CO₃ is lighter. In Na₂CO₃-NaHCO₃ solutions a basic Zn carbonate is deposited at active spots on the otherwise passive anode, whilst with high [NaHCO₃] 3Na₂CO₃·8ZnCO₃·8H₂O is formed (cubic, a 13.706 Å., d 2.726). No K-containing deposit is formed in K₂CO₃-KHCO₃ baths. The characteristics of the deposits are described and discussed in detail. J. W. S.

Passivity of iron and the Ostwald-Lillie concept of nerve conduction. III. Oscillographic investigations of the cathodic behaviour of passive iron and of platinum in nitric acid. H. Beinert and K. F. Bonhoeffer (*Z. Elektrochem.*, 1941, 47, 536—545).—Pt and Fe were cathodically polarised in HNO₃ by means of short current impulses from a 50-v. battery and the change in electrode potential with time was followed on a cathode-ray oscillograph. The experiments with

Pt served for comparison. The activating current does not of itself bring the Fe potential from the passive val. of ~ 1.0 v. to the activated val. of ~ 0.3 v. An intermediate potential of ~ 0.5 v. exists, and it is sufficient for the activating current to produce this val., when 10^{-4} coulomb has passed through the electrode. After interrupting the current at this stage, a potential lowering of ~ 0.15 v. takes place fairly rapidly, the Fe finally assuming the active state at a potential of ~ 0.3 v. The course of the potential-time curves depends on the kind of Fe used, temp., acid concn. and especially the HNO_3 content. The results can be explained by the assumption that a unimol. layer of surface oxide is partly reduced at the intermediate potential and the remainder is spontaneously reduced by local currents. After complete reduction the spontaneous decrease in potential occurs, which leads to activation. Studies of the activation of Fe in H_2SO_4 confirm this view. J. F. H.

Zinc plating from sodium zincate solutions.—See B., 1944, I, 31.

Anode reactions in the electrolysis of ethyl alcohol. E. Linde (5 *Nordiske Kemikermode*, 1939, 215—216).—Electrolysis of H_2O -free EtOH yields Et_2O_2 (I) and MeCHO (II) not by direct anodic oxidation but by: $\text{EtO}^+ \rightarrow \text{EtO} + e$; $2\text{EtO} \rightarrow$ (I); $\text{EtO} \rightarrow$ (II) + H. In presence of Na(K)OH or Na(K)OEt (II), $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHO}$, $\text{CHMe}\cdot\text{CH}\cdot\text{CHO}$, unidentified acids, ketones, and (probably) hydrocarbons, but not (I) or H_2 , are found. M. H. M. A.

Reduction of carbon dioxide during photosynthesis. J. C. McGowan (*Chem. and Ind.*, 1943, 458—459).—Explanations of CO_2 reduction during photosynthesis are discussed. The formation of an intermediate compound such as "methylene dioxide" is most probable, and a mechanism for the initial stages of photosynthesis is proposed. C. R. H.

Photochemical dimerisation of trans-cinnamic acid.—See A., 1944, II, 48.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Separate production of Glauber's salt and epsomite from natural astrakhanite. V. I. Nikolaev and A. I. Katschalov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 572).—If a solution of astrakhanite at 25° is cooled to $<0^\circ$, almost pure $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (I) is pptd. After pptn. of (I), brine containing MgCl_2 is added to the mother-liquor + MgSO_4 in the right proportions. Slight evaporation and cooling gives pptn. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. A. J. M.

Kurrol's sodium metaphosphate. H. Huber and K. Klumpner (*Z. anorg. Chem.*, 1943, 251, 213—220).—A new method for the prep. of Kurrol's insol. Na metaphosphate is described. Its m.p. is 630 — 650° , and ρ 2.6. Its properties are described; they differ in some respects from those recorded by Pascal (A., 1924, ii, 856). F. J. G.

Systems alkali oxide-CaO-Al₂O₃-SiO₂-CO₂. XI. Reaction pressures in the system $\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{CO}_2$. C. Kroger, K. W. Illner, and W. Graessner (*Z. anorg. Chem.*, 1943, 251, 270—284).—M.p. and X-ray diagrams for the system $\text{K}_2\text{CO}_3-\text{CaCO}_3$ under 50 atm. of CO_2 are given. A double carbonate $\text{K}_2\text{CO}_3 \cdot 2\text{CaCO}_3$, m.p. $\sim 835^\circ$, exists, and there are two modifications of $\text{K}_2\text{CO}_3 \cdot \text{CaCO}_3$. The dissociation pressures of these double carbonates are given. Reaction pressures and equilibrium data are given for systems consisting of K and Ca carbonates and double carbonates with SiO_2 and various K and Ca silicates and double silicates. F. J. G.

Effect of changes in lattice defect structure on the reactivity of cuprous sulphide. R. Jagitsch (5 *Nordiske Kemikermode*, 1939, 211—212).—Changes in the defect structure of Cu_2S on heating are independent of the history of the sample and are fully reversible. The reactivity of Cu_2S increases greatly around the transition temp., the material reacting explosively with O_2 . M. H. M. A.

Hydrothermal reactions. HI. Formation of calcium hydro-silicates from calcium oxide and silica gel at 300° and 350° and high pressures. W. Jander and B. Franke (*Z. anorg. Chem.*, 1941, 247, 161—179).—The formation of Ca hydrosilicates from SiO_2 gel and CaO in presence of excess of liquid H_2O at 300 — 350° has been studied. The products obtained are $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ ($n = 1.600$ and 1.612 ; cf. A., 1935, 50), $2\text{CaO} \cdot \text{SiO}_2 \cdot 0.5\text{H}_2\text{O}$ ($n = 1.658$ and 1.640), $\text{CaO} \cdot \text{SiO}_2 \cdot 0.25\text{H}_2\text{O}$ ($n = 1.586$), identical with xonotlite, and $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ ($n = 1.600$; cf. A., 1932, 707). F. J. G.

Chemistry and morphology of the basic salts of bivalent metals. X. Highly basic zinc hydroxychloride III. XI. Zinc hydroxybromides III and IV. W. Feitknecht and H. Weidmann (*Helv. Chim. Acta*, 1943, 26, 1560—1563, 1564—1569).—X. Addition of 45—80% of the equiv. amount of NaOH to 0.09M ZnCl_2 , followed by ageing of the ppt. for 5 months yields a product ("hydroxychloride III") with hexagonal lattice, a 6.30, c 7.77 Å., d 3.22; it corresponds with $4\text{Zn(OH)}_2 \cdot \text{ZnCl}_2$, with 34—38% of the Cl replaced by OH.

XI. Interaction of 0.25—0.8M ZnBr_2 with active ZnO, produced by the spontaneous dehydration of Zn(OH)_2 , yields a product ("hydroxybromide III") crystallising in hexagonal plates with a 6.32 and c 22.4 Å., and d 3.64. From its structure it is considered

to have the composition $3\text{Zn(OH)}_2 \cdot 2\text{Zn(OH)Br}$. Ageing of $\alpha\text{-Zn(OH)}_2$ in 0.05—0.18M ZnBr_2 yields a voluminous ppt. ("hydroxybromide IV") with a 3.145 and c 24.8 Å., which is regarded as comprising $\text{ZnBr}_2 \cdot 4\text{Zn(OH)}_2$ with $\sim 35\%$ of the Br replaced by OH.

J. W. S.

Boron. I. Preparation and properties of pure crystalline boron. A. W. Laubengayer, D. T. Hurd, A. E. Newkirk, and J. L. Hoard (*J. Amer. Chem. Soc.*, 1943, 65, 1924—1931).—Factors affecting the prep. of B by deposition on a glowing filament are discussed. Single crystals, in the form of needles or hexagonal plates, have been grown and optical evidence indicates that both types of crystals probably belong to the monoclinic system. Cryst. B exhibits great hardness, great opacity, metallic lustre, electrical properties usually associated with semi-metallic substances, and extreme chemical inertness. It is not attacked by boiling HCl or HF, but is slowly attacked by hot conc. HNO_3 , H_2SO_4 , or NaOH; it is slowly oxidised by heating to bright incandescence but oxidation is not sustained when the flame is withdrawn. The temp. coeff. of electrical resistance is \ll recorded vals. X-Ray diffraction patterns of the needle crystals show a spacing of 5.06 Å. along the needle axis with two equal and orthogonal axes 8.93 Å. in length lying perpendicular to the needle axis. Needle crystals are invariably interpenetration twins, with twinning along (130) and the needle axis in common. The needle crystals show an unusual amount of symmetry and this suggests that these crystals may be tetragonal under ideal conditions of crystal growth. Plate crystals show no twinning and the smallest cell based on orthogonal axes is a 17.86, b 8.93, c 10.13 Å. The structures of the two cryst. forms are not fundamentally different. The doubling of two of the corresponding translations in the needles cannot be fully explained. W. R. A.

Fluorination of boron trichloride. H. S. Booth and S. G. Frary (*J. Amer. Chem. Soc.*, 1943, 65, 1836—1837).—Only BF_3 is obtained when BCl_3 is fluorinated by SbF_5 in presence of SbCl_5 at 0° , -15° , -40° , and -78° or when BCl_3 and CaF_2 are heated up to 200° . No rearrangement occurs when BF_3 and BCl_3 are heated or subjected to electrical discharge. W. R. A.

Addition compounds of trimethylamine with boron fluoride and its methyl derivatives. A. B. Burg and (Miss) A. A. Green (*J. Amer. Chem. Soc.*, 1943, 65, 1838—1841).—The compounds $\text{NMe}_3 \cdot \text{BF}_3$ (m.p. $\sim 35^\circ$) and $\text{NMe}_3 \cdot \text{BFMe}_2$ (liquid) have been prepared. Their volatility and vapour-phase dissociation have been studied. The vapour of $\text{NMe}_3 \cdot \text{BF}_3$ is associated and does not dissociate at $<230^\circ$. Substitution of one Me for F in $\text{NMe}_3 \cdot \text{BF}_3$ leads to a large decrease in the strength of the N→B linking but further substitution of Me produces no marked diminution. The free energies of dissociation of the compounds have been estimated. W. R. A.

Volumetric determination of boric acid. IV. Activation of boric acid by polyhydroxy-compounds and processes for the volumetric determination of activated boric acid. H. Schafer (*Z. anorg. Chem.*, 1941, 247, 96—112).—The effective species in the titration of H_3BO_3 activated by polyhydroxy-compounds is the diol boric acid, $\text{H} \left[\text{R} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{B} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{R} \right]$. Other complexes play no significant part. An improved analytical procedure (C., 1944, Part 1) is described. F. J. G.

Boric acid and alkali borates. XI. System $\text{NaBO}_2-\text{H}_2\text{O}$. H. Menzel and H. Schulz (*Z. anorg. Chem.*, 1943, 251, 167—200).—Working details for the prep. of pure $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ (I) and $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ (II) are given. (I) is triclinic, with $\rho^{25} 1.743$. Vals. for the f.p. depression down to the cryohydric point (-5.77°) are recorded. From tensimeter curves the heats of hydration are $\text{NaBO}_2 \cdot 0.5\text{H}_2\text{O} \rightarrow$ (II), 13.9, and (II) \rightarrow (I), 12.55 kg.-cal. per g.-mol. of H_2O . The constitution of these salts is discussed. There is no justification for a dimeric formula. F. J. G.

Lower aluminium fluoride. W. Klemm and E. Voss (*Z. anorg. Chem.*, 1943, 251, 233—240).—When Al and AlF_3 are heated together in a vac. at 650 — 800° a volatile subfluoride $(\text{AlF})_x$ is formed; it decomposes on condensation to Al and AlF_3 . F. J. G.

Aluminium stearates.—See A., 1944, II, 3.

Rare-earth metal amalgams. IV. Isolation of europium. J. K. Marsh (*J.C.S.*, 1943, 531—535).—If Sm-Eu amalgam is decomposed with a mixture of H_2SO_4 and AcOH, mainly pure Sm(OAc)_3 and impure (20%) EuSO_4 are formed. If isolation of Eu is desired the crude rare-earth solution is treated with small amounts of H_2SO_4 and Na amalgam, when a ppt. of mixed EuSO_4 and SmSO_4 is formed, only a small amount of Sm-Eu amalgam being formed. Cold, dil. HNO_3 selectively oxidises SmSO_4 with formation of sol. $\text{Sm(NO}_3)_3$, leaving EuSO_4 (90%) which can be converted into $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$ by way of acetate, amalgam, and treatment with conc. HCl. Several methods of separating Sm from Eu after decomp. of amalgam where $\text{Eu/Sm} = 1/100$ have been tried and are described. C. R. H.

Mechanism of the combustion of carbon. V. Sihvonen (5 *Nordiske Kemikermode*, 1939, 96—112).—A review (cf. A., 1939, I, 570).

M. H. M. A.

Preparation of purified inorganic compounds for use in spectrographic standards. R. C. Hughes (*J. Opt. Soc. Amer.*, 1943, 33,

49—60).—Details of methods of purification of a no. of compounds are given. SiCl_4 is purified by repeated fractional distillation, and pure SiO_2 is obtained from it. Ca compounds are obtained by repeated extraction of impurities from $\text{Ca}(\text{OH})_2$ by H_2O , in absence of CO_2 , or by repeated recrystallisation of CaSO_4 . Mg compounds can be obtained by recrystallisation of MgSO_4 , and Na and K compounds by repeated volatilisation of the chlorides. The relative efficiency, convenience, and cost of various methods are compared.

A. J. M.

Preparation of properties of potassium thiogermanate and thiogermanic acid. H. H. Willard and C. W. Zuchli (J. Amer. Chem. Soc., 1943, 65, 1887—1889).—*K thiogermanate*, $\text{K}_2\text{Ge}_2\text{S}_5$, was prepared in solution thus: 2GeO_2 (hydrated) + $5\text{H}_2\text{S}$ + $2\text{KOAc} = \text{K}_2\text{Ge}_2\text{S}_5 + 2\text{AcOH} + 4\text{H}_2\text{O}$. Addition of COMe_2 gave two layers with AcOH and KOAc in the COMe_2 layer and a conc. aq. solution of $\text{K}_2\text{Ge}_2\text{S}_5$. Crystals of $\text{K}_2\text{Ge}_2\text{S}_5$ were deposited by abs. EtOH . Solid *thiogermanic acid*, $\text{H}_2\text{Ge}_2\text{S}_5$, was prepared thus: 2GeO_2 (hydrated) + $5\text{H}_2\text{S} = \text{H}_2\text{Ge}_2\text{S}_5 + 4\text{H}_2\text{O}$, but it was very unstable. The ion $\text{Ge}_2\text{S}_5^{2-}$ in acid solution yields a derivative with 5:6-benzquinoline.

W. R. A.

Reactions of solid substances. CXXXII. The course of sintering in lead powders followed dilatometrically. G. F. Hüttig and W. Hennig (Z. anorg. Chem., 1943, 251, 260—269).—The sintering of Pb powder shows itself as a contraction superimposed on the normal thermal expansion at $>100^\circ$. Foreign gases retard the process.

F. J. G.

Complex compounds and salts of ethylenediaminetetra-acetic acid. H. Brintzinger, H. Thiele, and U. Müller (Z. anorg. Chem., 1943, 251, 285—294).—The following compounds derived from ethylenediaminetetra-acetic acid $[\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2]_2 (= \text{RH}_4)$ are described: $\text{Pb}_2\text{R}_2\text{H}_2\text{O}$; $\text{Na}[\text{Co}^{\text{III}}\text{R}]_4\text{H}_2\text{O}$; $\text{H}[\text{Cr}^{\text{III}}\text{R}]$; $\text{H}[\text{Fe}^{\text{III}}\text{R}]$; $\text{NH}_4[\text{Fe}^{\text{III}}\text{R}]_2\text{H}_2\text{O}$; LaHR (I); NdHR ; $\text{ThR}_2\text{H}_2\text{O}$; $\text{ThR}_2\text{O} \cdot 5\text{H}_2\text{O}$; $\text{U}^{\text{IV}}\text{R}_2\text{H}_2\text{O}$. (I) is almost insol. in H_2O .

F. J. G.

Autoxidation of lead tricyclohexyl and its behaviour towards carbon tetrachloride.—See A., 1944, II, 65.

Fluorination of thiophosphoryl bromide. Thiophosphoryl bromofluorides. H. S. Booth and C. A. Seabright (J. Amer. Chem. Soc., 1943, 65, 1834—1835).—Fluorination of PSBr_2 with anhyd. SbF_5 , without a catalyst, yields PSF_2 and two liquids PSF_2Br and PSFBr_2 having the following vals.: b.p., $35.5 \pm 0.1^\circ$; $125.3 \pm 0.1^\circ$; f.p., $-136.9 \pm 0.5^\circ$; $-75.2 \pm 0.1^\circ$; ρ , 1.940; 2.390; heat of vaporisation, 6775; 8361 g.-cal.; Trouton's const., 22.0; 21.0; $\log p_0 \rightarrow 760 \text{ mm.}$, $-1484.8/T + 7.6970$; $-1827.3/T + 7.4674$. PSFBr_2 is less reactive than PSF_2Br and is unusually resistant to alkaline hydrolysis.

W. R. A.

Higher chromium fluorides (CrF_4 , CrF_5 , and CrO_2F_2). H. von Wartenberg (Z. anorg. Chem., 1941, 247, 135—146).— CrF_4 , CrF_5 , and CrO_2F_2 are described. CrF_5 is a brown amorphous solid, v.p. = 3 mm. at 220° , $\rho = 2.9$. The vapour is blue and has a characteristic absorption spectrum. CrF_5 is red and fairly volatile. Both are instantly hydrolysed by H_2O , affording Cr^{III} and Cr^{VI} . CrF_5 appears not to exist. CrO_2F_2 is formed as a brown gas; this condenses to a brown solid (v.p. = 24 mm. at 0°) which slowly changes to a white solid, not volatile at $<200^\circ$, apparently a polymeride. The absorption spectrum of the gas resembles that of CrO_2Cl_2 .

F. J. G.

Chromous iodide. F. Hein and G. Bähr (Z. anorg. Chem., 1943, 251, 241—250).—The work of Hein and Wintner-Hölder (A., 1932, 133, 229) has been confirmed. CrI_2 has 5.023. Its brown colour is not due to occluded I.

F. J. G.

Stability of uranium pentachloride. H. Martin and K. H. Eldau (Z. anorg. Chem., 1943, 251, 295—304).— UCl_5 dissociates appreciably into UCl_4 and Cl_2 at room temp. The dissociation tension is $<10^{-2}$ mm. at room temp. and $<10^{-1}$ mm. at 65° . The action of H_2O on UCl_5 is purely hydrolytic. The v.p. of UCl_5 at room temp. is $<10^{-2}$ mm.

F. J. G.

Nitroso-salts of the iron series. (A) L. Cambi. (B) W. Hieber and R. Nast. (C) L. Cambi (Z. anorg. Chem., 1941, 247, 22—30, 31—32, 33—34).—(A) Theoretical. The reactions and structures of Rousin's salts and analogous substances are discussed.

(B) A reply.

(C) A rejoinder.

F. J. G.

System NiTe—NiTe₂. W. Klemm and N. Fratini (Z. anorg. Chem., 1943, 251, 222—232).—Data on lattice const., ρ , and χ for Ni—Te preps. having compositions from NiTe to NiTe₂ are recorded. Different lattice const. are found for the same composition, the vals. falling into two series for which ρ is respectively $>$ and $<$ that calc. from the X-ray data. χ is small, indicating mainly a binding. Possible interpretations are discussed.

F. J. G.

Metallic amides and metallic nitrides. XII. System nickel-nitrogen. R. Juza and W. Sachsze (Z. anorg. Chem., 1943, 251, 201—212).—Ni nitride, Ni_3N , is obtained by heating Ni, NiF_2 , or NiBr_2 in NH_3 at 445° . It has a hexagonal close-packed lattice of Ni atoms with a 2.665, c 4.298 Å, c/a = 1.613, in the interstices of which the N atoms are accommodated; ρ_{25}^{25} 7.66. A structure

diagram is given. The solubility of N_2 in Ni is stable towards NaOH but is attacked by mineral acids. F. J. G.

Chemistry of bivalent and trivalent rhodium. V. Co-ordination complexes of rhodous halides with dialkylarsines. F. P. Dwyer and R. S. Nyholm (J. Proc. Roy. Soc. New South Wales, 1943, 76, 133—136; cf. A., 1942, I, 337).—The prep. of the following compounds is described: $[\text{RhX}_2(\text{AsMe}_2\text{R})_4]$ (I), $\text{X} = \text{I}$, $\text{R} = \text{Ph}$, m.p. $79-80^\circ$; $\text{X} = \text{I}$, $\text{R} = p\text{-C}_6\text{H}_4\text{Me}$, m.p. $80-82^\circ$; $\text{X} = \text{Br}$, $\text{R} = \text{Ph}$, m.p. $68-69^\circ$; $\text{X} = \text{Br}$, $\text{R} = p\text{-C}_6\text{H}_4\text{Me}$, m.p. $68-70^\circ$; $\text{X} = \text{Cl}$, $\text{R} =$

Ph and $p\text{-C}_6\text{H}_4\text{Me}$; $[\text{Cl}(\text{AsMe}_2\text{R})_3]\text{Rh}(\text{AsMe}_2\text{R})\text{Cl}$ (II),

$\text{R} = \text{Ph}$, m.p. 88° ; $p\text{-C}_6\text{H}_4\text{Me}$, m.p. $87-88^\circ$; $[\text{Rh}(\text{AsMe}_2\text{R})_3][\text{RhI}_2\text{AsMe}_2\text{R}]$ (III), $\text{R} = \text{Ph}$; $p\text{-C}_6\text{H}_4\text{Me}$, m.p. 207° ; $[\text{Rh}(\text{AsMe}_2\text{Ph})_3][\text{RhI}_2(\text{AsMe}_2\text{Ph})_2]$ (IV), m.p. 210° . (I) is formed by reduction of $[\text{RhX}_3(\text{AsMe}_2\text{R})_3]$ by H_3PO_3 in presence of AsMe_2R ; from its solution in aq. EtOH a compound of type (II) is pptd. under suitable conditions. (III) is formed by similar reduction of $[\text{Rh}(\text{AsMe}_2\text{R})_3][\text{RhX}_3]$, further reduction affording a compound of type (IV). (IV) is converted into (I) by dissolution in hot org. solvents; the reverse change occurs (incompletely) on boiling (I) with HX and H_2PO_3 .

A. J. E. W.

Constitution of Koefoed's nitroso-platinum complexes. K. A. Jensen (5 Nordiske Kemikermøde, 1939, 200).—The compounds obtained from NO or HNO_2 and solutions of various Pt complexes can also be prepared by addition of NOCl to the solids. In the green and blue salts, NO and Cl are separately linked in a 6-covalent complex cation, e.g., $[\text{Pt}(\text{NH}_3)_4(\text{NO})\text{Cl}]^{2+}$; the yellow forms have binuclear cations linked by the ON:NO group.

M. H. M.

XI.—GEOCHEMISTRY.

Characteristics of waters of underground lakes. G. A. Maximovitch and G. G. Kobjak (Compt. rend. Acad. Sci. U.R.S.S., 1941, 31, 26—28).—Chemical analyses of the waters of the lakes in the grottoes Titanic and Coliseum and of H_2O dripping from the cavern in Ethereal grotto are recorded. They show that the waters of underground lakes in gypsum-anhydrite rocks are to be classified as mineral waters.

L. S. T.

Cobalt in mine waters. I. P. Novochatski and S. K. Kalinin (Compt. rend. Acad. Sci. U.R.S.S., 1941, 31, 591—593).—Co is present in mine waters of a no. of deposits, particularly Cu and polymetallic deposits rich in Cu, thus indicating paragenesis of Co with Cu mineralisation. Mine waters serve as a concn. of Co. Owing to the presence of Mn compounds, Co is pptd. from solution at a lower pH than is normally required to ppt. it as hydroxide.

A. J. M.

Oxidation-reduction potentials and pH of the lake waters and of lake sediment. R. J. Allgeier, B. C. Hafford, and C. Juday (Trans. Wisconsin Acad. Sci., 1941, 33, 115—133).—Oxidation-reduction potentials and pH of lake H_2O are determined *in situ* (apparatus described). Redox potential is generally lower in the lower waters due not only to lower dissolved O_2 but also to Fe^{2+} , H_2S , and possibly org. reducing systems. Redox potentials of lake waters are not const.

L. G. G. W.

Beer's law and the proportion of organic matter in lake waters. H. R. James (Trans. Wisconsin Acad. Sci., 1941, 33, 73—82).—For a series of dilutions of lake H_2O , light absorption follows Beer's law so long as the dilution is $>5\%$. Below this irregular results are obtained because at these dilutions physical changes of the colloids in the H_2O take place.

L. G. G. W.

Isotopic composition of waters in metamorphic rocks and minerals. V. I. Vernadski, A. P. Vinogradov, and R. V. Teis (Compt. rend. Acad. Sci. U.R.S.S., 1941, 31, 573—576).—Chlorites, talcs, and serpentines of different deposits and geological ages were used. H_2O was distilled from them at 1140° , and its d determined. In almost all cases the d was $>$ that of standard purified tap- H_2O . In two cases, the greater d was shown to be due entirely to ^{18}O , the D content being $<$ that of standard H_2O .

A. J. M.

Sixteenth list of new mineral names. L. J. Spencer (Min. Mag., 1943, 26, 334—344).—A dictionary list of 94 names collected from the 1941—43 literature. Chemical formulæ are given for each mineral and a systematic chemical classification is appended.

L. J. S.

Helium indexes for several minerals and rocks. N. B. Keevil (Amer. J. Sci., 1943, 241, 680—693).—He index data for rocks and minerals from Franklin and Sterling Hill, New Jersey, and from Buchans, Newfoundland, and for diabases and basic rocks from Yellowstone National Park, Michigan, New Jersey, and Quebec, are recorded and discussed. He indexes for a series of cryst. basic rocks are fairly consistent with the expected geological sequence, probably because of the high He retentivities of the mafic constituents. Results for pre- and post-ore dykes in southern Quebec and Newfoundland indicate contemporaneous mineralisation in these two widely separated deposits. Rocks with a glassy groundmass are useless in geological correlation by the He method.

L. S. T.

Sulphur at Rotokaua, Taupo. J. Healy (*New Zealand J. Sci. Tech.*, 1942, 23, B, 84—92).—The S occurs in ores of several different types, the most common being patches of "massive" S, which consist of pure S embedded in a fine matrix of pumice. Lenses of "black" S (80% S) are closely associated with the massive deposits. The amount of S estimated to be available is $8-11.6 \times 10^6$ tons. All deposits are connected with thermal vents and are of volcanic origin, the S being deposited at the surface by oxidation of H₂S.

L. S. T.

Formation of mineral "hair silver." E. Jensen (5 *Nordiske Kemikermode*, 1939, 193).—"Hair Ag" (I) is formed whenever Ag is pptd. in presence of Sb⁺⁺⁺ in solution and a solid sulphide. (I) from Kongsberg (Norway) has been formed by migration of Ag⁺ in Ag₂S to a surface where it was pptd. by Sb⁺⁺⁺ or Cu⁺⁺ below 100°; it cannot have been formed by gaseous reduction of Ag₂S at >260°.

M. H. M. A.

Bauxite in Tasmania. H. B. Williams (*Bull. Imp. Inst.*, 1943, 41, 196—200).—Proved and potential resources at Ouse, Campbell Town, Swansea, and St. Leonards indicate a substantial vol. of ferruginous bauxite suitable for the production of Al. The Ouse deposits average Al₂O₃ 41.2, SiO₂ 3.2, and TiO₂ 2.17%.

L. S. T.

Nature and origin of Tasmanian bauxite. D. R. Dickinson (*Bull. Imp. Inst.*, 1943, 41, 200—203).—The physical characteristics of Tasmanian bauxites differ widely in the various localities, but the geological associations are similar, and the deposits probably belong to one epoch and were formed by similar processes, viz., decomp. *in situ* of volcanic tuff accumulations.

L. S. T.

Coloration of Ural corundums. B. A. Gavrusevitch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 686—688).—Coloration depends on genesis. Corundums from the Vishneviye Gory and Kishtym regions are greenish-grey and brown (pegmatites), greyish-blue and blue (desilicified pegmatites), and blue (emery deposits). The main colorants are Fe⁺⁺⁺, Fe⁺⁺, Ti, Mn, and, to a smaller extent, Ni and V, and they seem to replace Al isomorphously. Light corundums, except greyish-blue, have high content of Ca and Mg. Cr is absent in most and, when present, occurs to only a very limited extent.

W. R. A.

Composition of uraninites. R. Bakken and E. Gleditsch (5 *Nordiske Kemikermode*, 1939, 200—201).—UO₂: UO₃ in cleveite varies widely with different samples. UO₃ is formed from UO₂ and O₂ in solid solution from the transition: $2\text{UO}_2 \rightarrow 2\text{PbO} + \text{O}_2$ (PbO₂ is always absent), and UO₂:UO₃ is thus a very rough guide to the age of the mineral.

M. H. M. A.

Course of the reactions occurring between serpentine and superphosphate. H. O. Askew (*New Zealand J. Sci. Tech.*, 1942, 24, B, 128—134).—Reaction between ground serpentine (I) and superphosphate (II) leads to large reductions in the amounts of H₂O-sol. PO₄, CaO, and SO₄, but not to reductions in citric acid-sol. fractions; SiO₂ and Fe appear in a readily-sol. form. Since Ca₃(PO₄)₂ is the main Ca phosphate present after reaction is complete, the expected scheme $\text{Ca}(\text{H}_2\text{PO}_4)_2 + \text{MgO} = \text{CaHPO}_4 + \text{MgHPO}_4 + \text{H}_2\text{O}$ does not explain the reaction between (I) and (II). 2% citric acid extracts more Mg⁺⁺ from the mixture than does distilled H₂O. Mixtures of (I) and (II), originally moist, can become apparently dry without loss of total H₂O. This is due to hygroscopic H₂O being fixed as H₂O of crystallisation of the new phosphates formed during the reaction.

L. S. T.

Forgotten uses of selenite. C. E. N. Bromehead (*Min. Mag.*, 1943, 26, 325—333).—Mention is made of the use in ancient times of cleavage slabs of gypsum in windows.

L. J. S.

Genetic types of cobalt deposits in the Urals. A. E. Malachov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 148—149).—The most pronounced consens. of Co ores in the Urals occur in the following genetic varieties. (A) Deposits of the exogenetic group, represented by widely distributed deposits of the Mesozoic weathering crust of the Southern and Middle Urals, with types (i) hydroxide ores, with Co and Ni (1:6) contained in complex hydrated oxides of Fe, Mn, etc., and (ii) silicate deposits with Co and Ni (1:20) entering the isomorphous Mg silicates, revdiniskite, garnierite, etc. (B) Deposits of the endogenetic group, with types (i) silicate in dunite plutones of the Urals, with Co and Ni (1:10) entering olivines isomorphously, (ii) sulphide types present in classical deposits of the Urals, viz., Cu and Fe ore deposits, Cu pyrites deposits, hydrothermal Fe ore deposits, and altered rocks such as the listvenites of the Pishmin-Klutschevsk ore field. These sulphide types offer the greatest possibilities of utilisation.

L. S. T.

Occurrence of iron ore in the Catlins District, S. Otago. R. W. Willett (*New Zealand J. Sci. Tech.*, 1942, 23, B, 227—230).—The occurrence of Fe ore, cemented blacksand, in the Jurassic sandstone of this district is described. Two chemical analyses are given. The high TiO₂ content, ~8—9%, and the small quantity of ore eliminate economic possibilities.

L. S. T.

Tin in lievrite. G. P. Barsanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 594—597).—The occurrence of Sn has been confirmed in

a large no. of specimens of lievrite, so that its presence is not accidental. The processes by which Sn could be combined in a basic ferrosilicate mol. are discussed.

A. J. M.

Occurrence of indium in various metallogenic cycles of the U.S.S.R. N. M. Prokopenko (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 19—21).—In is an element typical of the metallogenic Variscian cycle. Its occurrence in this and other cycles is discussed.

L. S. T.

Distribution of indium in Ural ore deposits. S. A. Borovik and N. M. Prokopenko (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 22—23).—The distribution of In, which is frequent but variable in the pyrite and Cu—Zn deposits of the Urals is discussed.

L. S. T.

Prospecting evidence for indium. N. M. Prokopenko (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 16—18).—N. Kirghizia and E. Transbaikai can be regarded as enriched with In, whilst Altai and Salair are impoverished; the Urals occupy an intermediate position. Distribution of In in sphalerites (I) depends in an unknown way on the Fe concn.; In is more frequently contained in (I) from the lower horizons of a deposit. Black ferruginous (I) are especially rich in In. Prospecting for In should be conducted in polymetallic deposits of hypothermal, hypo-mesothermal, and mesothermal types, particularly sulphides.

L. S. T.

Content of germanium and other rare elements in topazes and beryls of the U.S.S.R. S. A. Borovik (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 24—25).—Spectrographic determinations of the Ge content of 28 samples of topaz (I) from different deposits of the U.S.S.R. are recorded. (I) of early origin shows a high Ge content; that of a later generation shows much less (10—20 times). Beryls (II) from the same deposits (Emerald mines) as the topazes with high [Ge] contains no Ge, but 0.01% of Sc and much Cr was present in the green (II). Chrysoberyl from this deposit contained 0.1% of Sn and comparatively much Ga. 9 samples of (I) contained no Ga, 1 contained ~10⁻⁴%, 10 contained 10⁻³%, and the remainder 0.005%. The distribution of Ga in the topazes is quite different from that of Ge. Some V and much Cr were present in the topazes that gave no Ge lines.

L. S. T.

Identity of tanatarite and diasporite. J. D. Gotman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 29—30).—The mineral found near Kairakty, Kazakhstan (Petrushkevitch, 1926) is a normal rhombic, and not a monoclinic, diasporite. Tanatarite does not exist, therefore, as a mineral species.

L. S. T.

Lazulite in the andalusite-sericite-quartz rocks of the Kongur-Alanghez range. S. A. Movsesjan (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 31—32).—The occurrence of lazulite (I) at Kapudshick is described, and a chemical analysis recorded. (I) is attacked by a mixture of any of the acids, HNO₃, HCl, H₂SO₄, H₃PO₄, and HF, only after ignition at 500—700°. It is unattacked by dil. H₂SO₄ (1:3) at high pressure (~32 atm.) or at 235°.

L. S. T.

Synthesis of magnesium silicate gels having a two-dimensional regular structure. H. Strese and U. Hofmann (*Z. anorg. Chem.*, 1941, 247, 65—95).—Gels obtained by boiling MgCl₂ and hydrated SiO₂ with KOH or Ca(OH)₂ have the composition and properties of Mg montmorillonite, Mg₃(OH)₂Si₄O₁₀·nH₂O. Hydrothermal treatment with KOH affords montmorillonite or mica according to conditions. Gels resembling antigorite, Mg₃(OH)₂Si₄O₁₀, may also be obtained under suitable conditions.

F. J. G.

Piedmontite-bearing quartz schists from Black Peak, N.W. Otago. C. O. Hutton (*New Zealand J. Sci. Tech.*, 1942, 23, B, 231—232).—Petrology is described, and optical data on the piedmontite and accessory tourmaline (elbaite) are recorded.

L. S. T.

Rare earths in scheelite. J. K. Marsh (*J.C.S.*, 1943, 577—578).—Chemical and spectroscopical analysis of scheelite from Forbes Reef, Swaziland, detects only 5% of the amount of Eu detected by Servigne's micro-method (cf. A., 1940, I, 303). Servigne's estimations of the amounts of other rare earths in scheelite are criticised.

C. R. H.

Thermochemical properties of the torbanite of the Glen Davis deposit. R. F. Cane (*J. Proc. Roy. Soc. New South Wales*, 1943, 76, 190—202).—Experimental investigation of the nature and rate of the thermal decomp. of torbanite (I) shows that there is no direct conversion of the original org. matter into crude oil and gas. The org. matter changes at a temp. < that necessary to produce oil into a semi-solid intermediate bitumen phase, which produces oil on decomp. Time and temp. are the two controlling factors in the nature of the oil produced. Data for thermal expansion, η , sp. heat, and heat of combustion of the crude oil obtained from (I) are recorded.

L. S. T.

Orepuki oil shale. R. F. Cane (*New Zealand J. Sci. Tech.*, 1942, 23, B, 212—216).—Physical characteristics and microscopic structure are described. Chemical analysis shows that the shale ash is typical, but the nature of the oil is less common. The higher fractions are largely saturated, and contain >10% of phenolic substances. S is high, and the oil contains large amounts of wax.

L. S. T.

A I—General, Physical, and Inorganic Chemistry.

MARCH, 1944.

I.—SUB-ATOMIC.

Continuous spectrum of hydrogen-like atoms (parabolical co-ordinates). W. R. Morgans (*Phil. Mag.*, 1944, [vii], 34, 842—850).—Theoretical expressions for the intensities for transitions between the continuous states and the Lyman and Balmer states are obtained from the solution of the wave equation in parabolical co-ordinates. H. J. W.

Continuous absorption of light in potassium vapour. R. W. Ditchburn, J. Tunstead, and J. G. Yates (*Proc. Roy. Soc.*, 1943, A, 181, 386—399).—A new type of absorption tube for the study of metal vapours is described. The continuous absorption of K and K₂ vapour in the range 3000—1600 Å. is studied, and the at. and mol. absorptions are separated. At short λ the at. absorption coeff. increases rapidly and varies linearly with ν . The at. results are in conflict with theory; it is suggested that exchange effects may account for the discrepancy. G. D. P.

Curves of growth for the A dwarfs, γ Geminorum and Sirius. L. H. Aller (*Astrophys. J.*, 1942, 96, 321—343).—The curves are constructed from measurements of equiv. widths of absorption lines of Fe I, Fe II, Ca I, Cr I, Cr II, Ti II, Sc II, and V II, a table of which is given. Excitation temp. ($\sim 6000^\circ$) and ionisation temp. (8700°) are derived. The electron pressure, 1.2×10^2 dynes (theoretical, 7×10^2), is calc. on the assumption that the broadening of the H lines is due entirely to continuous absorption by at. H in the stars. The amount of Fe above the photosphere of Sirius is 0.05 of that above the photosphere of the sun. H/Fe (by wt.) is ~ 1000 in the A dwarfs. E. R. R.

Survey of the spectra and radial velocities of the less regular M-type variable stars. A. H. Joy (*Astrophys. J.*, 1942, 96, 344—370).—The distribution, spectroscopic abs. magnitudes, spectral types, radial velocities, and displacements of emission lines are determined for 118 stars; spectroscopic observations on 105 of these are new. E. R. R.

Mean absolute magnitudes and space motions of the irregular variable stars. R. E. Wilson (*Astrophys. J.*, 1942, 96, 371—381). E. R. R.

Wave-lengths of new coronal lines. W. Petrie and D. H. Menzel (*Astrophys. J.*, 1942, 96, 395—398).— λ measured from three jumping-film, one ultra-violet moving-film, and five moving-film spectra of high dispersion, all photographed during the 1936 eclipse, are tabulated. New lines at 3980.9, 4003.5, 4056.3, 4170.8, 4272.9; 5899.1, 5912.4, 5937.1, 6294.9, 6336.9, 6513.0, 6524.1; 3216.5, 3296.1, 3577.2, 3586.6, 3630.7, 4429.8, 4674.4, 4705.7, 4783.9, and 5094.0 Å. were discovered. The last ten of these may arise from photographic effects of undetermined origin. E. R. R.

Composite spectrum of ζ Tauri. J. A. Hynck and O. Struve (*Astrophys. J.*, 1942, 96, 425—437). E. R. R.

Negative hydrogen ion and its absorption coefficient. R. E. Williamson (*Astrophys. J.*, 1942, 96, 438—450).—A six-parameter wave-function, derived on the basis of the Ritz principle, predicts an electron affinity of 0.0265 at. unit (current val. 0.0253) and an at. absorption coeff. of 3.0×10^{-17} sq. cm. at 5000 Å. (cf. 2.6×10^{-17} sq. cm. at 4000 Å.). The new vals. for the absorption coeff. are substantially $>$ the old throughout the red and infra-red. E. R. R.

Spectrographic observations of Nova Herculis (1934) and Nova Serpentis (1909) with identifications of [Fe V] and [Fe III] in Nova Pictoris (1925). P. Swings and O. Struve (*Astrophys. J.*, 1942, 96, 468—474).—Velocities of expansion of Nova DQ Herculis (1934) vary from 338 km. per sec. for [O II] to 256 km. per sec. for [O III], suggesting stratification. Lines show curved outer components, with a faint central line in the case of H γ . Since 1940 relative intensities of emission lines have changed considerably and the continuum of the central star has decreased in brightness. [Fe V] and [Fe VI] are well developed in the spectrum of Nova Serpentis, in which the electron density in the nebulosity is still high. E. R. R.

Interpretation of the spectrum of HD 190073. O. Struve and P. Swings (*Astrophys. J.*, 1942, 96, 475—480).—Beals' interpretation is discussed in the light of more recent measurements of the contours of the H and Ca I lines. E. R. R.

Spectrum of 67 Ophiuchi. P. Lacroute and W. H. Dirks (*Astrophys. J.*, 1942, 96, 481).—The spectrum, which is faint, was studied from 4100 to 4520 Å. During 28—29 July and 6—7 Aug., 1942, the star was of the P Cygni type. C II and O II lines were not observed either in emission or in absorption (see following abstract). E. R. R.

Spectrum of 67 Ophiuchi. O. Struve (*Astrophys. J.*, 1942, 96, 482).—Spectra taken in 1929—30, May, 1939, and 22 Sept., 1942, show no P Cygni structure (see preceding abstract). E. R. R.

Nuclear emission in spiral nebulae. C. K. Seyfert (*Astrophys. J.*, 1943, 97, 28—40).—Spectrograms of six extra-galactic nebulae with high-excitation nuclear emission lines superposed on a normal G-type spectrum are recorded. True relative intensities are deduced and individual differences discussed. Max. width of the Balmer emission lines increases with abs. magnitude of the nucleus and with the ratio of light in the nucleus to total light in the nebula. The wide emission lines are absent in the brightest diffuse nebulae in other extra-galactic objects. E. R. R.

Spectrographic study of meteorites. W. W. A. Johnson and D. P. Norman (*Astrophys. J.*, 1943, 97, 46—50).—18 meteorites were examined spectrographically for 69 elements. 40 were found, including As, Be, Cd, Ce, Hg, In, Ir, Pd, Pt, Te, Tm, and Zr, which are absent from King's list. No obvious grouping on the basis of at. constituents is possible. E. R. R.

Spectrum of τ Scorpii. P. W. Merrill and W. S. Adams (*Astrophys. J.*, 1943, 97, 98—104).—Total widths and displacements of lines of H, He, O, Ne, C, N, Mg, Al, Si, S, and Ca are measured with dispersion 2.9 Å. per mm. Total widths are H, 23 Å.; He, 1—8 Å.; others, 0.5 Å. Profiles and displacements of He lines strongly indicate the Stark effect. E. R. R.

Structure of interstellar H and K lines in 50 stars. W. S. Adams (*Astrophys. J.*, 1943, 97, 105—111).—Intensities of interstellar H and K lines of Ca II in 50 stars are measured. Radial velocity measurements may distinguish between different interstellar clouds, which appear to be of discrete nature, free from considerable turbulence, and of great extent. Intensities and displacements of additional narrow interstellar lines of Ca I, Fe I, CN, CH, and CH⁺ are measured. E. R. R.

Spectrum of the nebulosity near Kepler's Nova of 1604 [Nova Ophiuchi 1604]. R. Minkowski (*Astrophys. J.*, 1943, 97, 128—129).—The spectrum consists of emission lines of [O III] λ 5007, [O I] λ 6300, [N II] λ 6584, 6548, H α , and [S II] λ 6731 Å. The nebulosity may be a remnant of Kepler's Nova, which was a supernova. E. R. R.

Spectrum of Nova Cygni 1942. R. C. Sanford (*Astrophys. J.*, 1943, 97, 130—134).—Changes in the light and spectrum of this nova from Sept. 15 to Dec. 17, 1942, are recorded and compared with those of Nova Herculis 1934. E. R. R.

Emission-line intensities in some bright northern Wolf-Rayet stars. L. H. Aller (*Astrophys. J.*, 1943, 97, 135—165).—Excitation temp. of the atm. envelopes of certain bright Wolf-Rayet stars, estimated from emission line intensities, are very high and depend on the ionisation potential of the ion employed. The emission lines do not arise from the primary mechanism. The chemical composition of the atm. is deduced: in C stars, He/O=50, He/C=15; in N stars, He/N=20, He/C=300. These compositions indicate supernova rather than nova. Electron densities in the radiating layers of Wolf-Rayet stars are 10^{11} to 10^{12} electrons per c.c. E. R. R.

Spectrographic observations of peculiar stars. V. P. Swings and O. Struve (*Astrophys. J.*, 1943, 97, 194—225).—The spectrum of Z. Andromedæ in three successive years is tabulated. Strong lines of [Fe VII] were evident in July and Nov., 1942. New data on the emission lines of Fe I, Fe II, [Fe II], [Fe III], and [Fe V] in peculiar stars are given. Four stars with absorption shells are described in detail, especially shell lines of H and He I. Spectra of 83 Be stars are described: MWC 23 has a strong shell spectrum of H; MWC 342 shows strong emission lines of H, Fe II, and [Fe II], and shows structure in the H lines. The fluorescence and recombination mechanisms are related to the general characteristics of shell spectra. The "N flaring stages" of nova are discussed and related spectroscopic phenomena interpreted. E. R. R.

BD +14° 3887, a peculiar *Be* star showing emission lines of Na I, [Fe III], and He I, with a note on the spectrum of CD -27° 11944. J. W. Swenson (*Astrophys. J.* 1943, 97, 226—233).—BD +14° 3887 shows lines of H, Fe II, [Fe III], Cr II, Mg I, and Mg II, with an unusual combination of Na I, [Fe III], and He I. The mechanism of excitation of the emission lines is discussed. New lines, especially permitted Fe III multiplets $a^5P-4p^5P_0$ and $a^5D-4p^5P_0$, which are sensitive to dilution effects, are reported in CD -27° 11944.

E. R. R.

Spectrum of HD 192954. A. A. Broyles (*Astrophys. J.*, 1943, 97, 234—251).—Contours of H lines show very narrow and deep central cores with broad shallow wings to each side, indicating that part of the absorption occurs in a dense layer corresponding with a main sequence star, and part in a layer of low pressure. The weakening of Mg II and Si II lines indicates dilution in an outer layer. The star is probably of type B9n. λ of lines from λ 3321 to λ 5479 Å. are tabulated.

E. R. R.

Spectrum of ν Sagittarii in the visual region. J. S. Greenstein (*Astrophys. J.*, 1943, 97, 252—254).—The spectrum is marked by the strength of N and Ne lines. High Ne/O and abnormal N/O abundance ratios are estimated.

E. R. R.

Spectrophotometric observations of the light of the night sky. C. T. Elvey and (Miss) A. H. Farnsworth (*Astrophys. J.*, 1942, 96, 451—467).—Variations of intensities of lines at 5577, 6300, 6560, and 5893 Å. with zenith distance indicate a height of 500 km. for the auroral layer. Nocturnal variations of intensities were determined, and explanations suggested in the case of the Na line and the red O line (6300 Å.). The distribution of Na is exponential between 70 and 115 km.

E. R. R.

Observations of the light of the night sky with a photoelectric photometer. C. T. Elvey (*Astrophys. J.*, 1943, 97, 65—71).—Nocturnal variations include one with a min. near midnight and one in which intensity decreases throughout. Irregular variations which differ in different directions in the sky are reported. No positive results are obtained for the height of the atm., and motions of the irregular patches of light, and no relation is found between fluctuations in light and variations in the ionosphere as indicated by signal strengths of reflected radio beams.

E. R. R.

Time-lag of impulse breakdown at high pressures. J. D. Cobine and E. C. Easton (*J. Appl. Physics*, 1943, 14, 321—331).—Spark breakdown time lags are determined in N₂ at varying pressures (7—1000 lb. per sq. in.) and overvoltages 14—128% of the static breakdown voltage, for surges between Cu, Al, and Ni electrodes. Crit. pressure and overvoltage conditions, at which the lag changes abruptly from $\sim 10^{-2}$ to $\sim 10^{-5}$ — 10^{-6} sec., are found.

L. J. J.

Element 93 and its position in the periodic system. K. Starke (*Z. anorg. Chem.*, 1943, 251, 251—259).—Theoretical. Evidence for the view that element 93 has an outer electron configuration $5f6d^47s^2$, and represents the first of a series of "uranides" analogous to the rare earths, is discussed.

F. J. G.

Analytical chemistry of the rare earths. Average at. wt. of the rare earths in a mixture. G. L. Barthauer, R. G. Russell, and D. W. Pearce (*Ind. Eng. Chem. [Anal.]*, 1943, 15, 548—549).—The oxalate to oxide, oxalate to $KMnO_4$ method (cf. C., 1944, Part I) gives high vals. for the at. wts. of La, Nd, and Sm if the $KMnO_4$ is standardised against $Na_2C_2O_4$. The $KMnO_4$ must be standardised against a pure sample of the oxalate of the rare earth that is the most abundant constituent of any mixture under investigation.

L. S. T.

Separation of isotopes and thermal diffusion. J. Kendall (*Proc. Roy. Inst.*, 1942, 32, 296—309).—A lecture.

Applications of photographic methods to problems in nuclear physics. I (a) Determination of the energy of homogeneous groups of α -particles and protons. (b) Determination of the energy of fast neutrons. C. F. Powell (*Proc. Roy. Soc.*, 1943, A, 181, 344—359).—The relative advantages of the photographic method over the expansion chamber are discussed, and it is claimed that the advantages can be fully realised in practice.

(a) The range distribution is determined from the tracks of α -particles from Th and U. Protons are obtained by bombardment of B and Li targets with 500-kv. deuterons, and their photographically-determined range distribution is compared with results obtained with the counter method. The photographic method gives satisfactory agreement.

(b) Neutrons are obtained from Be and B by deuteron bombardment, and their energy is determined by observation of the tracks of "knocked-on" protons in the photographic emulsion. Satisfactory agreement with expansion-chamber results of other investigators is obtained. Neutrons from the transmutation of D and F are also examined.

G. D. P.

Measurement of the activity of radiosulphur in barium sulphate. R. H. Hendricks, L. C. Bryner, M. D. Thomas, and J. O. Ivie (*J. Physical Chem.*, 1943, 47, 469—473).—If pptd. $BaSO_4$ containing radioactive S is dispersed in EtOH and allowed to settle and the EtOH gently evaporated, a uniform deposit is obtained. Deposi-

tion of definite masses of ppt. on a polished brass disc and bringing the disc to a fixed position with respect to a thin counter window enables the activity of such ppts. to be measured quantitatively, very little activity being unavailable to the counter.

C. R. H.

Penetrating non-ionising cosmic rays. L. Jánossy and G. D. Rochester (*Proc. Roy. Soc.*, 1943, A, 181, 399—408).—Experiments already briefly reported (cf. A., 1942, I, 129) prove the existence of a penetrating non-ionising radiation at sea-level having a mean range of 10 cm. in Pb. It is probably the same as the radiation discovered by Rossi and Regener (A., 1941, I, 145) at 4300 m. above sea-level. The radiation may consist of neutrons.

G. D. P.

Origin of cosmic rays and duration of existence of atoms. V. G. Fesenkov and N. N. Pariiski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 191—194).—From the intensity of cosmic rays it is calc. that the half-life of an "average atom" is $\sim 1.6 \times 10^{17}$ years.

J. J. B.

II.—MOLECULAR STRUCTURE.

Tentative identification of the Herzberg bands of O₂ in the ultra-violet spectrum of the night sky. P. Swings (*Astrophys. J.*, 1943, 97, 72—74).—The strong night-sky bands between λ 3110 and 4174 Å., including the strongest ultra-violet feature at λ 3556 Å., are identified with bands of Herzberg's system $^3\Sigma_u^+$ in agreement with Dufay.

E. R. R.

Profiles in the alpha band of atmospheric oxygen. H. A. A. Panofsky (*Astrophys. J.*, 1943, 97, 180—185).—Seven lines were photographed with the Berkeley solar spectrograph and interferometer and their profiles measured. Consistency, and agreement of the results with theory, indicate no serious errors in the interferometric method. The total absorption coeff. of the α band, computed by two methods, was 8.7×10^4 and 9.4×10^4 per sec. per cm. of normal atm. The mean mol. diameter for collision between O₂ mols. and air mols. was estimated to be 5.15×10^{-8} cm.

E. R. R.

Resolution of the telluric bands ω_1 and ω_2 . A. Adel (*Astrophys. J.*, 1943, 97, 190—193).—The CO₂ bands ω_1 and ω_2 in the solar spectrum (20,061, 20,568 Å.) are resolved into their rotational structures, and observational data for the two branches of each band are tabulated.

E. R. R.

Absorption spectra of *o*-dichlorobenzene. K. Siddiqi (*Current Sci.*, 1943, 12, 253).—With a H₂ discharge tube as ultra-violet source, 12 absorption bands in the region 2799—2596 Å. were obtained under optimum conditions (14 mm. pressure and 24°). Data for λ and ν are tabulated.

N. M. B.

Complete analysis of absorption spectra. VI. Physico-chemical properties of the chromophoric naphthalene nucleus. E. Hertel (*Z. Elektrochem.*, 1941, 47, 813—819; cf. A., 1943, I, 296).—The absorption spectra of the following compounds have been determined over the range 15,000—40,000 cm.⁻¹: α - and β -C₁₀H₇NH₂, 1- and 2-C₁₀H₇NO₂, β -C₁₀H₇OH, 1:2-, 1:4-, 1:5-, and 1:8-C₁₀H₈(NH₂)₂, *o*- and *p*-NO₂C₆H₄NH₂, 1:2-, 6:2-, 8:2-, 1:4-, 2:1-, and 5:1-NO₂C₁₀H₈NH₂, and 1:5- and 1:8-C₁₀H₈(NO₂)₂. The dipole moments of some of these compounds, together with some others, have been determined or re-determined. The relationship between absorption spectra and dipole moments is discussed. If two groups are substituted in the same nucleus of C₁₀H₈, the effect on absorption spectrum and dipole moment is very similar to that produced in C₆H₆. If two similar substituents are introduced into different nuclei, the absorption spectrum is additive but distorted. With two dissimilar substituents in different nuclei, there is a small displacement of the absorption range if the variochrome activity of the substituents is small. If it is greater, the long- λ absorption range is displaced far into the visible. The effect on colour of introducing NO₂ in different positions of *p*-dimethylaminobenzene-1-azonaphthalene has been investigated by means of absorption spectra.

[A. J. M.]

Absorption spectrum of luciferin and oxidised luciferin.—See A., 1944, III, 138.

Preparation and absorption spectra of five pure carotene pigments.—See A., 1944, II, 74.

Special characteristics and configurations of stereoisomeric carotenoids including polyycopene and pro- γ -carotene.—See A., 1944, II, 40.

Colour matching.—See B., 1944, II, 41.

Chemistry of sulphur. I. Raman spectrum and constitution of hydrogen disulphide. F. Feher and (Fr.) M. Baudier (*Z. Elektrochem.*, 1941, 47, 844—848).—The Raman spectrum of carefully purified H₂S₂ corresponds completely with that of H₂O₂, and the constitution of the two mols. is therefore similar. An assignment of frequencies to S-S and H-S linkings is made.

A. J. M.

Ultra-violet luminescence of crystals of alkali halides activated by heavy metals. A. M. Polonski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 543—545).—The position, form, and intensity of the ultra-

violet luminescence bands of alkali halides containing Cu, Ni, and Ag ions are investigated, rock-salt and artificial KCl, NaBr, and RbCl crystals being used. The introduction of Cu⁺⁺ or Ni⁺⁺ into the lattice of NaCl and KCl does not affect the position and form of the fluorescence bands of crystals coloured by X-rays. The introduction of Ag⁺ on the other hand, gives a very intense ultra-violet luminescence, the bands of which agree with the radiation from the unactivated crystals. NaCl and KCl, activated by Ag⁺, also show an intense ultra-violet phosphorescence. NaBr and RbCl, which, in the pure state, show no ultra-violet luminescence, give a very intense one on introduction of Ag⁺. A. J. M.

Electrical moment of metallo-organic compounds. II. Silicon triethyl and triphenyl hydroxide; silicon triethyl chloride and oxide. L. Malatesta and R. Pizzotti (*Gazzetta*, 1943, 73, 143—148).—The electrical moments of SiEt₃Cl, SiEt₃OH, (SiEt₃)₂O, and SiPh₃OH are slightly < the moments of the corresponding C compounds. This is attributed chiefly to the capacity of the Si atom to take up > eight electrons in the outer shell. J. F. M.

Nature of molten salts.—See A., 1944, I, 63.

Dielectric properties of Buna synthetic rubbers.—See B., 1944, II, 55.

Influence of thin dielectric films on the magneto-optical Kerr effect in ferromagnetic mirrors. M. M. Noskov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 111—112).—Films of nitrocellulose, bakelite, or paraffin oil on Ni, permalloy, or Fe increase the magnetic rotation effect to a max. of ~100%, followed by a decrease with increasing film thickness. The field-dependence of the increased effect follows the change of the normal effect in a magnetic field, reaching saturation at the same val. of the field. Explanations are reached. N. M. B.

Physical properties of l(+)- and d(-)-alanine.—See A., 1944, II, 35.

Rotatory dispersion of α-amino-acids.—See A., 1944, II, 70.

Constitution of glass. B. Schweig (*Glass*, 1943, 20, 173—174, 200—202, 227—229, 236, 257—259, 285—287, 313—314, 318; 1944, 21, 7—11).—A review of at. structure leading to the appraisal of glass-forming and glass-stabilising anions and cations in terms of their ionic potentials (i.e., valency/ionic radius) and their ρ-val. (i.e., ionic radius/at. radius). On the basis of the σ-val. (i.e., valency of cation × (radius of anion)^{1/2}/valency of anion × (radius of cation)^{1/2}), the various oxides fall uniformly into groups of glass formers, stabilisers, and modifiers, without the overlapping of the group σ-val. The theories of the structure of the glassy state are briefly described. J. A. S.

Effect of resonance on the force constants and lengths of chemical bonds. E. Warhurst (*Trans. Faraday Soc.*, 1944, 40, 26—39).—An equation is derived showing the effect of resonance on bond length, and is applied to resonance between covalent single and double bonds, and to that between covalent and ionic bonds. A second equation shows how the bond force const. is affected by resonance, and is used to explain the decrease in vibration frequency observed when certain gases are liquefied or dissolved in non-ionising solvents. For HCl, HBr, HI, and H₂ the calc. magnitudes of this effect agree with experimental data. F. L. U.

Molecular wave functions for lithium. C. A. Coulson and W. E. Duncanson (*Proc. Roy. Soc.*, 1943, A, 181, 378—386).—The method of mol. orbitals is applied to the discussion of the ground state of Li. The final energy val. has an error of ~1.3%. The changes in screening consts. in passing from at. to mol. states are discussed and empirical rules deduced. G. D. P.

Application of Polya's theorem to optical, geometrical, and structural isomerism. W. J. Taylor (*J. Chem. Physics*, 1943, 11, 532).—The applications described by Hill (A., 1943, I, 220) can be extended. The result of the calculations of the nos. of three types of isomerides of cyclopropane is given as an example. L. J. J.

Physical properties and chemical constitution. VIII. Alkyl chlorides, bromides, and iodides. A. I. Vogel (*J.C.S.*, 1943, 636—647; cf. A., 1943, I, 117).—*n* has been determined for a wide range of alkyl chlorides, bromides, and iodides, for the C, D, F, and G' lines, at 20.0°. γ and ρ have also been determined, over a range of temp.; [R] and parachors have been calc., and the CH₃ differences evaluated from the results for *n*-halides. The CH₃ difference in parachors is 40.10 from the data for chlorides, 40.02 for bromides, and 39.98 for iodides, differing somewhat from the accepted val. (39.0). A. J. M.

Surface tension of white phosphorus.—See A., 1944, I, 12.

Surface energy and heat of vaporisation.—See A., 1944, I, 12.

III.—CRYSTAL STRUCTURE.

Structure of electrodeposited chromium. W. Hume-Rothery and M. R. J. Wyllie (*Proc. Roy. Soc.*, 1943, A, 181, 331—344).—The appearance and crystal orientation of electrodeposited Cr are c 2 (A., 1.)

studied with c.d. of 50—3000 amp. per sq. ft. in the temp. range 12—85°. In the brightest deposits a (111) plane is parallel to the surface. The residual stress in the deposit is least when the brightness and preferred orientation are greatest; the hardness is also max. for these deposits. G. D. P.

Reflexion of X-rays from the "anti-phase nuclei" of AuCu₃. A. J. C. Wilson (*Proc. Roy. Soc.*, 1943, A, 181, 360—368).—The superlattice lines in the X-ray spectra of AuCu₃ are not always sharp; the breadth depends on the indices of the line. The effect is due to the way in which the superlattice is organised in different parts of the crystal. Calculations are made of the line broadening to be expected on five assumptions regarding the way in which the nuclei "change step." Closest agreement with observations is given by a manner of "changing step" in which Au atoms avoid one another. G. D. P.

X-Ray study of the dissociation of an alloy of copper, iron, and nickel. (Miss) V. Daniel and H. Lipson (*Proc. Roy. Soc.*, 1943, A, 181, 368—378).—Unusual diffraction effects are observed when the alloy Cu₃FeNi₂ is in process of dissociating into two face-centred cubic structures. Each line in the spectrum is accompanied by side bands. Although complete agreement with theory is not obtained it appears that the cubic lattice is deformed by segregation of the atoms in the early stages of the dissociation. The segregation occurs with a periodicity of ~50 unit cells, so that a modulation of the structure is produced. The changes which the alloy undergoes will probably elucidate the mechanism of dissociation in alloys in general. G. D. P.

Crystal chemistry of alloys. U. Dehlinger and G. E. R. Schulze (*Z. Metallh.*, 1941, 33, 157—160).—In metallic compounds in which the valencies are not fully saturated each metallic bond between two atoms corresponds with a definite energy of formation, and hence an increase in the co-ordination no. of the lattice implies a greater heat of formation and therefore greater thermal stability. This principle explains the composition, structure, and stability of CuMg₂ and MgZn₂-type phases, the structure of AlB₂, CuAl₃, and similar compounds, and the preference of heteropolar metallic compounds for the composition AB and a body-centred cubic structure; the electrical conductivity of the AB type of metal compounds shows that an equally strong metallic bond is superimposed on the heteropolar bond. A. R. P.

X-Ray diffraction studies on precipitated cuprous and cupric sulphides. H. B. Weiser, W. O. Milligan, and J. M. Marshall, jun. (*J. Physical Chem.*, 1943, 47, 496—501).—Cu₂S prepared by pptn. with H₂S from solutions of Cu₂Cl₂ and CuS similarly prepared from solutions of CuCl₂ give chalcocite and covellite X-ray diffraction patterns, respectively. Copptd. sulphides give both patterns, with no indication of the presence of digenite. Ageing the ppts. under H₂O at room temp. has little effect, except to form traces of CuSO₄·5H₂O if air has not been excluded. Ageing at 90° increases the primary particle size. C. R. H.

Crystalline structure of zinc cyanide. H. S. Shdanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 352—354).—The lattice is cubic, *a* 5.89 Å.; 2 mols. per unit cell; space-group *T*_h². A. J. M.

Crystal structure of silver oxalate. R. L. Griffith (*J. Chem. Physics*, 1943, 11, 499—505).—X-Ray diffraction data show that Ag₂C₂O₄ crystals are monoclinic, with the space-group *P*₂/C—*C*_{2h}. The unit cell has *a* 3.46 ± 0.02, *b* 6.16 ± 0.02, *c* 9.47 ± 0.04 Å., β 76 ± 1°, with 2 mols. of Ag₂C₂O₄. All atoms are in sets of fourfold general positions. The structure can be considered as an assemblage of chain mols., (Ag₂C₂O₄)_n, parallel to the *b* axis, held together by Ag—O linkings. The *x*, *y*, and *z* parameters found for the atoms are, respectively: Ag 0.145, 0.495, 0.156; C —0.070, 0.115, —0.012; O¹ 0.163, 0.216, —0.110; O² —0.163, 0.187, 0.100. L. J. J.

Crystal structure of braunite.—See A., 1944, I, 72.

Morphology of the finest lead oxide sublimates. III, IV. R. Meldau and M. Teichmüller (*Z. Elektrochem.*, 1941, 47, 630—634, 634—636).—III. Very fine PbO sublimates dissolve in H₂O at room temp. and deposit hexagonal crystals of Pb(OH)₂. Electron-micrographs of salmon-coloured PbO show the frequent occurrence of crystals closely resembling those of Pb₃O₄.

IV. Very fine PbO₂ sublimates are unaffected by H₂O. They have a large sp. surface with only traces of cryst. structure. Very fine Pb sublimates slowly oxidise in air at room temp. to PbO in the form of pseudomorphs of the original Pb crystals. Sublimates having the approx. composition Pb₃O show crystal angles resembling those of Pb and PbO; there is no evidence for the existence of Pb₂O. F. J. G.

Relations between silicates, phosphates, and sulphates. R. Klement (*Z. Elektrochem.*, 1941, 47, 843—844).—The isotypy and isomerism occurring among silicates, phosphates, and sulphates is discussed with special reference to the compounds Na₂Ca₄(SO₄)₆, K₂Ca₂SiP₂O₁₂, Ca₂Si₃P₂O₂₀, and Na₂CaS₂O₂₀. From analogy with the isotypy of titanite, CaTi(SiO₄/O), and tilasite, MgCa[AsO₄/F],

it is assumed that isotopy also exists between disthene, $\text{AlAl}[\text{SiO}_4/\text{O}]$ (triclinic), and amblygonite, $\text{LiAl}[\text{PO}_4/\text{F}]$ (triclinic). The powder diagrams of the last two show some similarities. A. J. M.

Crystal structure of ethylene. C. W. Bunn (*Trans. Faraday Soc.*, 1944, 40, 23—25).—Reconsideration of published data leads to the following details for the structure of solid C_2H_4 : unit cell orthorhombic, a 4.87, b 6.46, c 4.14 Å. Space-group $Pnmm$ (D_{2h}^{12}). Coordinates of C atoms: (1) $x\bar{y}0$; (2) $x\bar{y}0$; (3) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}$; (4) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}$, where $x=0.11a$ and $y=0.06b$. The interat. distances agree with those found in related substances. F. L. U.

Diffraction of X-rays by sodium laurate and sodium palmitate at higher temperatures. O. E. A. Bolduan, J. W. McBain, and S. Ross (*J. Physical Chem.*, 1943, 47, 528—535).—Fibre photographs of the supercurd, subwaxy, and waxy cryst. phases of Na laurate (I) and palmitate (II) obtained over the range 25—155° show that the three phases are respectively stable at the following approx. temp.: (I) 85°, 112°, 153°; (II) 85°, 120°, 155°. The existence of the transition curd supercurd at ~70° for (I) is indicated. C. R. H.

Structure and thermal properties of crystals. V. Thermal expansion of phthalocyanines and porphins. A. R. Ubbelohde and (Miss) I. Woodward (*Proc. Roy. Soc.*, 1943, A, 181, 415—427).—H. Pt, and Cu phthalocyanines are investigated by X-ray methods at 90—600° K. The thermal mol. movements in the crystals are calc. Apparatus, including a new design of furnace for use with X-ray cameras and single crystals, is described. G. D. P.

Diamond. (Sir) R. Robertson (*Chem. and Ind.*, 1944, 18—24).—Jubilee memorial lecture.

Change of colour and optical properties of beryls on heating.—See A., 1944, I, 71.

Development of stresses in the bonding of single crystals and polycrystalline metals. U. Dehlinger, A. Kochendorfer, H. Held, and E. Lorcher (*Z. Metallk.*, 1941, 33, 233—235).—The load-bending curve for Zn single crystals shows a well-marked point of inflexion; this behaviour may be explained by assuming that flow begins in the outer layers immediately the normal elastic limit is reached, but proceeds unchecked only after application of a greater bending moment. Al single crystals behave similarly, but the point of inflexion is less marked and the bending moment required to cause plastic deformation is for Zn. Polycryst. Al, Cu, and steel behave similarly when the yield point is exceeded. A. R. P.

Orientation of grains of recrystallisation in zinc crystals. V. A. Solotov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 186—190).—When plates from a single crystal of Zn are bent so as to induce twinning, and then annealed at 350°, the preferred orientation of the new crystal grains agrees with that of the twinning axis. Single Zn crystals bent and heated at 350° show a strong recrystallisation, but it is much reduced if the bent crystals are first kept at 150° and then annealed at 350°. J. J. B.

Vitreous state. Semiquantitative considerations. M. L. Huggins (*J. Physical Chem.*, 1943, 47, 502—511).—Theoretical. Equilibrium between cryst. and non-cryst. conditions in a solid or liquid and the rate of attaining equilibrium are considered as functions of net energy changes for small internal structural rearrangements, of the activation energies of such rearrangements, and of temp. Annealing, devitrification, and stability of vitreous substances are considered from this viewpoint. Slow cooling through all crit. regions of structural change is essential for max. stability. Rapid cooling results in the "freezing-in" of some relatively unstable at. distributions which will cause strains and inhomogeneities, and which may not resolve into a stable structure for a very long time. C. R. H.

Theory of elastic properties of rubber.—See B., 1944, II, 54.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Mol. wt. and composition of high polymers.—See B., 1944, II, 55.

Magnetic properties of crystalline horse-radish peroxidase and its derivatives.—See A., 1944, III, 138.

Absorption of ultrasonic waves in viscous liquids. P. A. Bashulin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 113—116).—For not too viscous liquids, discrepancies between experimental absorption- ν vals. and those calc. by Stokes' formula taking account only of the normal η coeff. can be explained with the help of the second η' coeff. regarding viscosity as a relaxation phenomenon. Absorption measurements for ultrasonic waves in glycerol containing 50% of H_2O and in castor oil show in the former case fair agreement, and in the latter case wide divergence from calc. vals. Explanations in terms of relaxation theory are discussed. N. M. B.

Specific heat of carbon dioxide. C. S. Venkateswaran (*Current Sci.*, 1943, 12, 252—253).—The intense sharp Raman line at 58 cm^{-1} for solid CO_2 is attributed to coherent rotational oscillations of mols. in the crystal lattice. This is supported by application of the

Raman theory of sp. heat; the vals. for C_p calc. for the range 15—100° K. from frequencies corr. for low temp. are in close agreement with observed vals., showing that the Raman theory is applicable to mol. compounds. N. M. B.

Thermal behaviour of micro- and macro-molecular substances and its modification. K. Ueberreiter (*Kolloid-Z.*, 1943, 102, 272—291).—The properties of a substance in any state of aggregation are determined by the freedom of motion of its mols. In liquids the thermal energy of mols. is sufficient to overcome the potential barriers surrounding them. In cryst. solids the potential barriers are all of similar magnitude; in amorphous bodies they differ, hence the melting process is not sharp, and a place-exchange occurs below the m.p., resulting in increased orientation. The f.p. of amorphous bodies is determined experimentally as the point of intersection of sp. vol.—temp. curves for solid and liquid. In a macromol. liquid the chain members are more strongly influenced by their neighbours in the same chain than by those in other chains. The relative magnitudes of inter- and intra-mol. forces determine whether chains move as a whole, or whether chain units move relatively to one another. The relation of chain length to f.p. shows that large mols. must be subdivided into small kinetic units having varying degrees of thermal agitation. The state in which the kinetic energy is distributed among chain members but not whole mols. is described as a liquid with fixed structure (I). Its range of existence is greater the greater is the chain length. Macromol. substances are classified according to their thermal properties into (i) rubber-like polymers, with weak intramol. forces and wide temp. range of (I), (ii) thermoplastics, with smaller and higher temp. range of (I), and (iii) non-softening polymers, with small or no range of (I). Intramol. movement is limited by electrostatic forces, and modification of physical properties necessitates modification of electric moments, especially of side-groups or chains. E.g., chlorination of polyvinyl chloride or replacement of Cl by ester groups lowers the f.p. by compensation or reduction of dipole moments. Internal mobility may be increased or decreased by netting of chains, according to its effect on the dipoles. External plasticisers reduce intramol. forces and so increase the mobility of chain members. R. H. F.

Viscosities and rheochors of nitric acid, nitro-paraffins and their isomeric nitrites. J. N. Friend and W. D. Hargreaves (*Phil. Mag.*, 1944, [vii], 34, 810—816).—Measurements of ρ and η for HNO_3 and the first six nitro-paraffins and their isomeric nitrites (except $\text{MeO}\cdot\text{NO}$) lead to vals. of the rheochors (R). Using previously determined vals. for C, O, and H, R can be calc. for NO_2 and $\text{O}\cdot\text{NO}$. The effect of the co-ordinate bond is to decrease R from a mean val. 39.3 to 38.9. For HNO_3 the measured R is in agreement with the val. calc. on the assumption that the NO_2 group is not dissociated. H. J. W.

Structure mechanics of viscous elastic systems. VI. Viscosity and chemical constitution of micromolecular systems. H. Umstätter (*Kolloid-Z.*, 1943, 102, 232—245).—By substitution of the time parameter in the Maxwell elasticity law by the corresponding quantity in Newton's law of cooling, an equation connecting viscosity and temp. at const. vol. is obtained. The integration limits are the upper and lower crit. temp., the latter corresponding with that temp. at which the liquid no longer flows but breaks, and the transition from solid to liquid occurs without heat intake. From the surface tension (γ) and the shearing elasticity (E), calc. from the deduced equations, the linear dimensions of micromols. can be calc. from $r=2\gamma/E$ to 0.75 Å. or better. The relaxation time (τ) can be calc. from γ and the abs. mol. wt. (m) from $\tau^2=m/2\gamma$. Compounds with approx. equal τ -vals. dissolve each other well. Mol. cohesions can be compounded additively at corresponding temp., as is shown at half the crit. temp. From measurements of mol. refraction, the "mean" formulæ (in terms of no. of double bonds and rings) of a series of technical hydrocarbon mixtures are determined. J. F. H.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Viscosity of normal paraffin solutions. Viscosity and structural relations of linear polymers. A. R. Kemp and H. Peters (*Ind. Eng. Chem.*, 1943, 35, 1108—1112).—The viscosities (η) of solutions of n -paraffins from $\text{C}_{10}\text{H}_{22}$ to $\text{C}_{28}\text{H}_{58}$ in C_6H_6 , CCl_4 , $n\text{-C}_8\text{H}_{18}$, CHCl_3 , and cyclohexane have been measured at 20°. Only in C_6H_6 is the sp. $\eta \propto$ the length of the C chain, as demanded by the Staudinger relation. Consideration of the contribution to the η of chain atoms has led to the development of a new η const. $K_{ca} = \log \eta W / \Phi N$ (W = proportional wt. of chain atoms in repeating unit to base mol. wt., Φ = vol. concn., N = no. of C atoms in the chain). Vals. for K_{ca} lie between 0.030 and 0.038 (mean 0.032) and use of the mean val. permits calculation of chain length in polymers. The η of solutions of stearic and palmitic acids in $n\text{-C}_8\text{H}_{18}$ indicates that they exist as double mols. whereas their esters occur as single mols. J. W. S.

Changes in an osmotic system during freezing. G. Galos (*Bio-dynamica*, 1941, 3, 209—216).—When a Cellophane bag containing

sucrose solution was immersed in the same sucrose solution and the outer solution frozen, H_2O passed from the inner to the outer solution during the freezing. L. G. G. W.

Dielectric constant of mixed systems. R. Vieweg and T. Gast (*Z. tech. Physik*, 1943, 24, 56—62).—Parameters in the formulae for ϵ of two-phase mixed systems are evaluated by measurements in systems in which one phase is invariable in distribution and properties while the ϵ of the other is varied. This effect is produced by compression of air in the interstices of a porous mass. The ϵ of a material in powder form can be determined in this way. L. J. J.

Structural mechanics of viscous-elastic continua. VIII. Kinetics of aggregation of molecular disperse systems. H. Umstätter (*Kolloid-Z.*, 1943, 103, 150—159).—The variation of results obtained from mol. wt. determinations of substances of high mol. wt. in solution is due to the presence of groups capable of free rotation, which can behave as if they were dissociated from the mol. On the other hand, strongly unbalanced mols. can aggregate on account of the compensation of their intramol. energy differences, thus behaving kinetically as if they were associated. The viscous properties of solutions are more often due to aggregates than to the mols. themselves. A. J. M.

Fluidity of electrolytes. II. E. C. Bingham and R. T. Foley (*J. Physical Chem.*, 1943, 47, 511—527).—Available data on the η of mixtures of electrolytes have been examined. Better agreement between observed and calc. vals. is obtained if it is assumed that fluidities and not η are additive. Fluidity data* for mixtures of $N-KCl$ and $-NaCl$ at 25°, $N-NaNO_3$ and $-KNO_3$ at 10°, 20°, and 30°, and 0.05N-LiF and $-KI$ at 25° are tabulated. A new determination of the ionic fluidity elevation of Pb shows that the positive val. calc. from Grüneisen's data (cf. *ibid.*, 1941, 45, 885) is incorrect, the correct val. being —28.2. C. R. H.

Anion rotation in crystal lattices of A.BX₃ compounds. M. A. Bredig (*J. Physical Chem.*, 1943, 47, 587—590).—The existence of a thermal effect without a change in crystal symmetry, which has been observed in solid solutions of Na_2SO_4 and K_2SO_4 , is ascribed to a second-order transition from oscillation to rotation of the SO_4^{2-} anions at high temp. C. R. H.

Standard nomenclature of magnesium alloy microstructures. A. Fisher (*Magnesium Rev.*, 1943, 3, 31—38).—In the system of nomenclature adopted, the names given to the different types of structure are those used to describe similar structures in steel. Typical photomicrographs are given. C. E. H.

Orientation of precipitated beta phase in relation to that of parent alpha grain in Elektron AZ91. E. Lardner and J. Nelson (*Magnesium Rev.*, 1943, 3, 39—41).—From X-ray and microscopical evidence, it is concluded that the thin plates of β , pptd. from the super-saturated solid solution of Al in Mg on ageing above 200°, lie flat on the basal planes (0001) of the α grains. C. E. H.

Constitution of the lead-antimony and lead-antimony-silver systems. B. Blumenthal (*Amer. Inst. Min. Met. Eng.*, 1943, *Tech. Publ.*, 1634, 11 pp.; *Met. Tech.*, 1943, 10, No. 6).—The solidification of Pb-Sb alloys was studied by thermal analysis, cooling rapidly at 12—18° per min., and stirring vigorously. Supercooling was observed with hypereutectic alloys and could not be entirely prevented even by vigorous stirring at slow rates of cooling. The eutectic is placed at 252° with 11.1% of Sb. Supercooling was also observed in Pb-Sb-Ag alloys. This system has a ternary eutectic with 11.4% of Sb and 1.4% of Ag at 244.7° $\pm 0.5^\circ$. Invariant equilibria are assumed to exist at 272° and 297°. J. C. C.

Nickel-molybdenum system. F. H. Ellinger (*Trans. Amer. Soc. Met.*, 1942, 30, 607—638).—The constitutional diagram was determined from metallographic and X-ray data, using alloys made by sintering or melting briquetted mixtures of H₂-reduced powders in H_2 . A eutectic occurs between Ni-rich α solid solution and the δ phase ($NiMo$) at 1320° with 46.5% of Mo; δ (62.5% of Mo) is formed from Mo-rich ϵ solid solution by a peritectic reaction at 1370°. At 1370°, ϵ dissolves 0.9% of Ni. At 1320°, α dissolves 37% of Mo, the solubility falling to 30% at 890° (when a peritectoid reaction occurs with the formation of γ , Ni_3Mo), to 23% at 840° (when another peritectoid reaction produces β , Ni_2Mo), and to 20.5% at 600°. Alloys with 21 to 35% of Mo, quenched from 1300°, age-harden on heating at 600—800°. J. C. C.

Magnetic investigations in the ternary system, aluminium-chromium-copper. A. Knappwost and H. Nowotny (*Z. Metallk.*, 1941, 33, 153—157).—Alloys of the ternary system with >30% Al were examined by X-ray, magnetic and micrographic methods. Al dissolves 3.1% of Cr at 600°. With more Cr the compound Al_3Cr separates, but with 30—50 at.-% of Cr a body-centred cubic phase with superlattice is formed; this phase has a 3.035—3.000 Å. In the ternary system no ternary compounds are formed but the γ Cr-rich solid solution dissolves a max. of 10 at.-% of Cu and the γ Cu-rich solid solution only a small amount of Cr. The ternary diagram contains two broad ternary fields: $Al_3Cu + Al_3Cr + \gamma$, and

$Al_3Cu + \gamma + \gamma'$, a broad binary field of $\gamma + \gamma'$, and two narrow binary fields: $Al_3Cu + Al_3Cr$ and $Al_3Cu + \gamma$. Al_3Cu is non-magnetic, the γ phase is strongly diamagnetic, and the other phases are paramagnetic. A. R. P.

New temperature-sensitive magnetic alloy. F. W. Ackermann (*Z. tech. Physik*, 1943, 24, 45—46).—Magnetic properties of materials can be made dependent on temp. by utilising the effect of internal mechanical stresses, e.g., a material for which μ increases with temperature can be made from a Ni-invar bimetallic strip in which deformation with change of temp. is prevented. This has μ increasing approx. linearly from 7 at —100° to 31 at 100° at 3 oersted. L. J. J.

X-Ray study of the hysteresis effect observed in the palladium-hydrogen system. E. A. Owen and E. St. J. Williams (*Proc. Physical Soc.*, 1944, 56, 52—63; cf. A., 1937, I, 560).—Investigations in the range 60—130° of the hysteresis effect observed when the pressure is varied show definite relations between the temp. and certain crit. vals. of the pressure connected with the appearance and disappearance of the two phases present in the system. The α -phase lines in the structure spectra were initially sharp, but, on reappearance of the phase with decreasing gas pressure, were diffuse; the β -phase lines were always diffuse. N. M. B.

Correlating adsorption data. D. F. Othmer and F. G. Sawyer (*Ind. Eng. Chem.*, 1943, 35, 1269—1276).—Plots of equilibrium v.p. of adsorbed substances against concn. (Freundlich isotherms) are not straight lines, even on a logarithmic plotting. They may be replaced by plotting equilibrium pressure against normal v.p. of the same or a similar substance in accordance with the Dühring system, but using a logarithmic plot. In general the new relationship is expressed by a straight line or by two intersecting lines indicating a change of state at the intersection. By suitable choice of a reference substance, plots may be continued beyond the crit. point of the adsorbed material. From the slope of the lines (isosteres) a measure of the instantaneous heat of adsorption may be obtained, and shown to agree with experimental vals. F. Rb.

Adsorption of vitamin-C. A. Kuhn and H. Gerhard (*Kolloid-Z.*, 1943, 103, 130—135).—Untreated C adsorbs ascorbic acid (I) with simultaneous oxidation. The adsorption does not follow Boedecker's adsorption formula, $x = K(C-x)^n$, where C = initial concn., x = mass adsorbed, K and n are consts. Pre-treatment of the C with reducing agents (Na_2S , $Na_2S_2O_4$, etc.) reduces the extent of oxidation considerably. The presence of Fe in the C is less important. Boedecker's formula holds for (I) and dehydroascorbic acid when the C has been treated as above. Floridin, bentonite, and frankonite adsorb very little (I) from HPO_3 solution, and there is some oxidation. Fuller's earth adsorbs somewhat, without oxidation. A. J. M.

Surface tension of *n*-heptane and *n*-butane containing dissolved nitrogen. G. J. Reno and D. L. Katz (*Ind. Eng. Chem.*, 1943, 35, 1091—1093).—The surface tensions of $n-C_7H_{16}$ and $n-C_4H_{10}$ saturated with N_2 at 200, 500, and 1000 lb. per sq. in. pressure have been measured at 25°. Measurements with C_7H_{16} solutions were also made at 55° and 85°. From the results it is inferred that the parachor [P] of N_2 in $n-C_4H_{10}$ is 60, in accord with the val. for liquid N_2 , but that when dissolved in C_7H_{16} [P] = 41. J. W. S.

Surface tension of sodium soap dispersions in mineral oils. W. Gallay and I. E. Puddington (*Canad. J. Res.*, 1943, 21, B, 225—229).—Addition of Na oleate (I) and Na stearate (II) to mineral oils does not affect the surface tension (γ) until a certain temp. is reached [greater for (I) than for (II) in the same polar oil], when they cause a sharp decrease. The decrease for a polar is > that for a non-polar oil, and addition of glycerol (III) as well as the soap causes a greater decrease but it occurs at the same temp. The γ -temp. relation is linear in all cases and the additions do not affect the temp. coeff. In the polar oil, additions of excess of fatty acids and alkali as well as (II) act similarly to (III) but the alkali raises the temp. at which γ decreases. The effects are related to the physical state of the soap in the dispersions (cf. A., 1944, I, 32). J. H. Ba.

Wetting power in sodium soap-mineral oil systems. W. Gallay, I. E. Puddington, and J. S. Tapp (*Canad. J. Res.*, 1943, 21, B, 230—235).—The contact angle of mineral oils on Na stearate (I) and oleate (II) is independent of the viscosity index of the oil but is the less the smaller is its viscosity. In general the angle at (I) is < at (II). Oils of low viscosity index show a lower interfacial tension against H_2O and greater emulsion stability. The presence of glycerol (III) on the surfaces increases the spreading of the oil, and in (III)-soap gels the oil will displace the (III) to a certain extent. Such a displacement occurs in industrial soap-base lubricating greases, (III) existing as droplets in the oil. J. H. Ba.

Pseudo-optics in capillary phenomena. R. E. Liesegang (*Kolloid-Z.*, 1943, 103, 95—96).—When dye solutions are allowed to rise in paper through capillary action patterns are formed by the pptd. dye. If barriers, in the form of cuts in the paper, are put in the path of the capillary rise, patterns resembling optical patterns are obtained. Coloured photographs are given. A. J. M.

Movement phenomena in the precipitation of dissolved substances of high mol. wt. F. H. Müller (*Kolloid-Z.*, 1943, 103, 144—145).—If a drop of fairly dil. solution of polystyrene in C_6H_5OAc is dropped on to H_2O , it immediately spreads out, forming a thin film, but after a short time circular movements take place, and the film suddenly contracts considerably with crinkling. For conc. solutions the crinkling takes place more slowly. Phenomena of a similar kind with other substances are described. They are unaffected by impurities on the surface, or in the bulk of the H_2O . The effect is modified when the solution is poured on to a glass surface. An explanation involving orientation of the polystyrene chains is given. A. J. M.

Structure of collodion membrane and its electrical behaviour. VII. **Water uptake and swelling of collodion membranes in water and solutions of strong inorganic electrolytes.** C. W. Carr and K. Sollner (*J. Gen. Physiol.*, 1943, 27, 77—89; cf. A., 1943, I, 180).—Dried collodion (I) membranes swell reversibly when placed in H_2O to an extent varying from 5 to 11% according to the brand of (I). The uptake of H_2O and swelling of oxidised (I) are the same as those of the original unoxidised (I), and hence the CO_2H that are introduced in the oxidation have no detectable effect on swelling. There is a very small negative temp. coeff. of swelling, and swelling at 50° is $\sim 13\%$ < at 3° . The uptake of H_2O as determined by increase in wt. is > can be accounted for by the increase in vol., and swelling accounts for only 60—70% of the H_2O taken up by the membrane. When " H_2O -wetted dried" (I) membranes are transferred from H_2O to solutions of strong electrolytes there is no detectable change in vol., and under similar conditions there is no significant change in vol. with "porous" membranes. When dried (I) membranes swell in H_2O some of the H_2O becomes "bound" and both intra- and inter-micellar swelling seem to occur, and hence neither the increase in wt. or in vol. nor their difference is a measure of the true pore space of the membrane. It is concluded that the abs. H_2O content is not so important as the proportion of H_2O in the H_2O -wet membranes that is available in useful ways for the different solutes. J. N. A.

Capillary activity and colloidal gas. R. Auerbach (*Kolloid-Z.*, 1943, 103, 136—137).—The effect of capillary-active substances on changes of state of gas dispersions has been investigated. Such substances (e.g., $iso-C_6H_{11}OH$) favour the formation of colloidal gases, and prevent their coagulation or dissolution. A. J. M.

Results of aerosol research in science and technology 1932—1942. I, II. K. A. G. Meyer (*Kolloid-Z.*, 1943, 102, 293—298; 103, 65—71).—A short review covering the more academic aspects of the work. The subjects discussed include terminology, prep., stabilisation, measurement of particle size, coagulation by ultrasonic waves, filtration, and adsorption. J. F. H.

Ionic exchange in colloid sulphur. I. E. O. K. Verstraete (*Kolloid-Z.*, 1943, 102, 251—267).—A preliminary investigation of the prep. and conditions of stability of S sols. Both Raffio and Selmi sols were used. The two sols are similar. A method is described for the determination of the polythionic acids present (both as free acid and as salts), which enables the process of ageing to be investigated. The degree of dispersion of the S sols was also determined. The coagulation vals. (C.V.) of $LiCl$, HCl , $NaCl$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, $Al(NO_3)_3$, $Th(NO_3)_4$, and hexol nitrate for the Selmi sol were determined (order of decreasing C.V.). For anions the order of decreasing C.V. is $S_2O_3^{2-}$, SO_4^{2-} , ClO_4^- , Cl^- , NO_3^- , CO_3^{2-} . Dilution of the sol leads to greater C.V., which is not in agreement with previous authors. H_2S decreases the stability of the sols. It shows a characteristic influence on the C.V.; in general the univalent metals are unaffected, for 2- and 4-valent metals the C.V. decreased, for Al and K increased. H^+ ions lower the charge on the S, whilst OH^- ions cause a slight initial rise in the electrokinetic potential up to neutralisation. Na^+ depresses the ζ -potential and the sol is discharged long before it is pptd. The appearance of the coagel and the reversibility or irreversibility of the coagulation caused by various cations were investigated. J. F. H.

Study of dispersed systems by progressive desiccation. J. V. Rubio and M. Amat (*Anal. fis. quim.*, 1943, 39, 332—350).—Two varieties of $Cr(OH)_3$ peptised by ClO_4^- are partly separated by ultrafiltration into two parts which behave differently on progressive desiccation. F. R. G.

Recognition of various types of bentonite. H. Erbring and H. Lehmann (*Kolloid-Z.*, 1943, 103, 126—129).—The η of suspensions of 3 bentonites (from U.S.A., Italy, and Germany) in cyclohexanol has been determined by a rotation viscometer. The η -concn. curves of the U.S.A. and German specimens lie very close together, but the η of the Italian bentonite is > that of the other suspensions at the same concn. The method may be used for identification. A. J. M.

Effect of concentration and pH on the viscous and electrochemical properties of hydrogen bentonites. J. N. Mukherjee, N. C. Sen Gupta, and M. K. Indra (*J. Physical Chem.*, 1943, 47, 553—577).—The sp. conductivity of dil. suspensions of H bentonites increases linearly with concn. (C) except at high C when it increases much

more rapidly. The equiv. conductivity, after being approx. const., rapidly diminishes and passes through a min. At this C the cataphoretic velocity, which increases with C, passes through a max. The equiv. conductivity calc. from pH is > that observed. The extinction coeff. diminishes with C and then rises to a max. η increases with C would be expected from a linear relation on account of the particles being non-spherical and non-rigid and the effective vol. of the particles varying with C. The apparent sp. gr. increases with C to a const. val. which agrees with the sp. gr. of dried bentonite. The data suggest that increase in C causes aggregation and that the aggregates form a structure possessing yield val. C. R. H.

Electrochemical properties of clay minerals and the differentiation of hydrogen clays and bentonites by electrochemical methods. I. Kaolinite and kaolinitic clays. J. N. Mukherjee, R. P. Mitra, and D. K. Mitra. II. Montmorillonitic clays and bentonites. R. P. Mitra, S. N. Bagchi, and S. P. Ray (*J. Physical Chem.*, 1943, 47, 543—549, 549—553).—I. Titration curves and other electrochemical features of kaolinite and kaolinitic clays from Dacca lateritic soils have been investigated and are discussed. At both inflexion points the base-exchange capacities of kaolinite are in the order $Ca(OH)_2 > NaOH > Ba(OH)_2$, but for a given pH the order is $Ca(OH)_2 > Ba(OH)_2 > NaOH$. The data for the clays show that kaolinite is the dominant mineral constituent of the Dacca lateritic soil.

II. Similar examination of montmorillonite from Padegaon (Bom-bay) and of two bentonites from Hati-Ki-Dhani (Jodhpur) and Bhadres has been undertaken. The second clay behaves as a strong or moderately strong dibasic acid towards NaOH, the other clays being weakly monobasic; towards $Ca(OH)_2$ and $Ba(OH)_2$, however, the first clay behaves as a strong monobasic acid. C. R. H.

Theory of thixotropy. W. von Engelhardt (*Kolloid-Z.*, 1943, 102, 217—232).—Theoretical. The series of liquids of increasing thixotropic activity, obtained by Winkler (A., 1939, I, 77) using kaolin, is the same as that obtained by the author (*Nachr. Akad. Wiss. Göttingen, Math.-phys. Kl.*, 1942) in an investigation of the abrasive hardness of quartz in various liquids, the quartz being hardest in liquids where the thixotropy is greatest. The degree of thixotropy (T) is defined as the ratio vol. of liquid : vol. of solid in a suspension that gels in 1 min. Between the solid particles of a rigid gel are assumed attractive and repulsive forces, the latter decreasing the more rapidly with distance. The distance (d) between the particles is related to the quantity of liquid held in the gel and hence to T. The repulsive forces are attributed to the electrical charge on the solid particles, which causes a polarisation of the liquid. The stronger is the polarisation, the less is d and therefore the less is T. Non-polar liquids are polarised least and therefore T is greatest in them. The dependence of T on the solid phase is determined in the first instance by the shape of the solid particles. A gel of plates will contain more liquid than one of spheres if the d vals. are the same. It is shown that the d vals. for a gel containing plates and for one containing spheres, with radius equal to that of the plates, are of the same order; the only assumptions made are that the attractive forces are of a van der Waals nature and that the repulsive forces are due to surface charges. J. F. H.

Viscosity of suspensions. (Effect of strong electrolytes on the viscosity of starch and bentonite suspensions.) A. von Buzagh (*Kolloid-Z.*, 1943, 103, 119—126).—The η of starch (I) and bentonite (II) suspensions have been determined at various concns. up to 20 g. per 100 c.c. and are compared with those of quartz (III) suspensions. For suspensions with charged particles the η -concn. curve is convex to the concn. axis, but for (I) and (III) suspensions with isoelectric particles, η varies linearly with concn. With (II) suspensions the curve is convex to the concn. axis, as for charged particles. (I) and (III) suspensions show no structural η in either the charged or isoelectric state, though this is found for (II) suspensions. The relation between η , cohesion, and cataphoretic migration velocity has been investigated for the three suspensions in the presence of a no. of strong electrolytes. In the case of hydrophobic suspensions (quartz and starch), electrolytes affect η and cohesion in a similar manner. There is a max. of both quantities at the isoelectric point. The cation only is effective with quartz suspensions, but both ions are effective with starch. For (II) there is no connexion between η and cataphoretic velocity. Ostwald's activity coeff. law holds for (I) and (III), but not for (II). A. J. M.

Theory of elastic properties of rubber.—See B., 1944, II, 54.

Statistical mechanics of cross-linked polymer networks. I. Rubber-like elasticity. II. Swelling. P. J. Flory and J. Rehner, jun. (*J. Chem. Physics*, 1943, 11, 512—520, 521—526).—I. Expressions are derived for the structural entropy and entropy change on deformation of a network of polymer chains with random cross-linkages. The cross-linkages are treated as if situated at the common apices of a series of regular tetrahedra.

II. Statistical mechanical treatment of swelling in solvents on the basis of the authors' model shows that max. swelling depends on the degree of cross-linking, and its temperature coeff. can be

used to calculate the heat of interaction with the solvent. Swelling capacity should be diminished by the application of external stress, and the modulus of elasticity should decrease inversely with the cube root of the swelling vol. L. J. J.

Statistical thermodynamics of rubber. III. F. T. Wall (*J. Chem. Physics*, 1943, 11, 527—530; cf. A., 1942, I, 204).—Expressions for the distribution of mol. lengths in strained rubber, and equations of state for rubber-like materials, are derived. L. J. J.

Statistical treatment of imperfectly flexible chains. H. M. James and E. Guth (*J. Chem. Physics*, 1943, 11, 531).—Mathematical methods applicable to a quant. treatment of the authors' mol. model of rubber (B., 1944, II, 54) are indicated. L. J. J.

Influence of adsorbed gases on hydrogen-ion concentration of frozen and thawed solutions of synthetic high polymers. L. Holzapfel and F. F. Nord (*Biodynamica*, 1940, 3, 1—9).—Solutions of polyacrylic acid (I), polyvinyl alcohol (II), and polymethacrylamide (III), frozen after CO_2 , N_2 , O_2 , or H_2 had been bubbled through them and then thawed, showed an altered pH. O_2 decreased the pH of (I) solutions after freezing at all concns. of the acid, and $>0.001\%$ of H_2 and N_2 decreased it at low but increased it at high concns. N_2 increases at low and decreases at high concns. the pH of (II), but gives the reverse effect with (III). At all concns. CO_2 decreases the pH of solutions of these substances. Solutions treated with CO_2 , frozen, thawed, and then treated with N_2 showed no effect of the CO_2 on the pH. It is suggested that foods frozen in a CO_2 atm. should be thawed in a N_2 atm. L. G. G. W.

Statistical theory of chain configuration and physical properties of high polymers. P. J. Flory and J. Rehner, jun. (*Ann. New York Acad. Sci.*, 1943, 44, 419—429).—The distribution of distances between chain ends in polymers with flexible mols. is unaffected by a symmetrical hindrance potential with regard to rotation about bonds. Steric effects in long mols. are not symmetrical, and hindrance to rotation then increases the distance, but the form of the distribution function is unchanged. Methods of calculating elastic moduli of materials with network structures from the change of entropy are discussed, and a statistical treatment is given avoiding simple assumptions of change in chain length distribution on deformation. Swelling by solvents is a combination of osmotic dilution opposed to elastic reaction. Equations are derived for the concn. of cross-linkings from the equilibrium degree of swelling. R. H. F.

Elasticity and flow in high polymers. R. Simha (*Ann. New York Acad. Sci.*, 1943, 44, 297—312).—The elastic properties of a crystal and a liquid are contrasted with those of rubber-like materials. The latter are distinguished from other high polymers both by the val. of elastic deformation and by the rate of attainment of equilibrium. An equation describing the total deformation as composed of ordinary elastic extension, a reversible deformation established gradually, and a viscous flow is examined in detail. The equations reproduce approx. experimental data on creep curve and effect of temp. on deformation for various times of loading and frequencies. The behaviour is not characterised by a single time const. but by a range of relaxation times. The process of relaxation is discussed, and the case of two mechanisms with different relaxation times is examined. The effect of temp. on elasticity is principally on the time effects. Analogies are drawn between mechanical deformation and thermal expansion. The relations do not apply if crystallisation occurs on deformation. R. H. F.

Rigidities of solutions of polymers. J. D. Ferry (*Ann. New York Acad. Sci.*, 1943, 44, 313—327).—Rigidity is complicated by relaxation of stress at const. strain, viscous flow in series with elastic deformation, delayed elastic recovery, and variation of rigidity with frequency of applied stress. These can be partly accounted for by the Maxwell concept of viscous deformation in series with elastic deformation. Methods of and difficulties in determining rigidities are described, and results are discussed for solutions of polybutene in heptane, polystyrene in xylene, and plasticised polyvinyl chloride and polymethyl methacrylate. Two mechanisms for support of shear are the orientation entropy of long-chain mols. and the bending of C—C bonds in immobilised mols. At high concns. intermol. attractions must be considered. A mechanical model, the elements of which can be identified with mol. processes, is described to represent the behaviour of the polystyrene-xylene system. R. H. F.

Absorption of light by, and particle size in, humus colloids. F. Pickenbrock (*Kolloid-Z.*, 1943, 103, 146—150).—Na humate solutions from various sources, extracted with $\text{Na}_2\text{C}_2\text{O}_4$ or NaOH, were brought to different pH vals. by addition of NaOH or $\text{H}_2\text{C}_2\text{O}_4$, and their extinction coeffs. were determined before and after centrifuging at 3000 and at 15,000 r.p.m. A considerable part of the deepening of colour produced by addition of alkali was removed by centrifuging at the higher speed, but not at the lower. The colour deepening is due to a large extent to the commencement of coagulation, which, however, does not proceed further owing to the stabilising effect of Na^+ and OH^- . A. J. M.

Structure-viscosity of mucin and a new apparatus for its measurement. P. Zamboni (*Kolloid-Z.*, 1943, 102, 246—251; cf. C., 1944, Part I).—A viscometer is described which enables the time of outflow to be measured at various pressures and is especially suitable for the investigation of "fibrocolloids." Structure viscosity is especially marked in solutions of mucin, but is not observed in presence of salts in sufficient concn. The salt concns. necessary are of the same order as those required for the activation of mucin-dissolving enzymes. J. F. H.

Production of chain-like aggregates during coagulation. K. Hoffmann (*Kolloid-Z.*, 1943, 103, 161—163).—The coming together of colloidal particles to form chain-like aggregates is ascribed to the different field distribution at the ends and side surfaces of the components of the chains. A. J. M.

VI.—KINETIC THEORY. THERMODYNAMICS.

Equilibrium problems [in chemical kinetics] with more than one solution. P. Oesper (*J. Chem. Educ.*, 1943, 20, 511).—Two examples are discussed. L. S. T.

Hydrolysis of chlorine. G. B. Kolhatkar and U. A. Sant (*J. Univ. Bombay*, 1943, 12, A, Part 3, 57—59).—Conductivity measurements show that the equilibrium $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HOCl}$ is very rapidly attained from either direction, thus confirming the findings of Schilov *et al.* (A., 1936, 1345). H. W.

Potential barriers in ethyl alcohol and the equilibrium in the reaction $\text{C}_2\text{H}_5 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{OH}$. J. G. Aston, G. J. Szasz, and S. Isserow (*J. Chem. Physics*, 1943, 11, 532—534).—EtOH can exist in "straight" and "bent" forms with a difference of 1560 g.-cal. per mol. for E_0 . Using the val. -52,090 g.-cal. per mol. for ΔE_0 in the reaction $\text{C}_2\text{H}_5(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{C}_2\text{H}_5\text{OH}(\text{g})$, free energy changes and equilibrium consts. at 298.2—600° K. are calc. as $\Delta F^\circ = -1565$, +15, +1570, +7488, at 298.2°, 351°, 403°, 600° K., respectively, in improved agreement with experimental vals. L. J. J.

Effect of temperature change on ionisation constants of weak electrolytes. H. O. Jenkins (*Trans. Faraday Soc.*, 1944, 40, 19—22).—A new equation, $\log K = A/T + B(\log T)/T + C(\log^2 T)/T + D$, is proposed, which fits experimental vals. for aq. HCO_2H , AcOH , EtCO_2H , and PrCO_2H as well as do those of Harned and Robinson (A., 1940, I, 412) and Everett and Wynne-Jones (*ibid.*, 73); it also involves relationships for ΔH and ΔC_p that are more in accordance with expectation than those given by existing formulae. F. L. U.

Thermodynamic properties of solutions of high polymers: empirical constant in the activity equation. M. L. Huggins (*Ann. New York Acad. Sci.*, 1943, 44, 431—443).—The thermodynamic activity of each component in a solution of flexible long-chain mols. in a small-mol. solvent is expressed as a function of the partial molal vols. by a formula involving an empirical const. μ_1 characteristic of the pair of components. μ_1 is related to the heat of mixing and to the lack of perfect randomness of mixing (aggregation or solvation); it is only slightly dependent on the flexibility of chains. A linear relation between μ_1 and the reciprocal of the abs. temp. is deduced, and confirmed by data on polystyrene-alkyl laurate gels. In many cases μ_1 is independent of concn. Vals. of μ_1 for a large no. of systems are tabulated. R. H. F.

Principles of Carnot and Clausius. W. Wilson (*Phil. Mag.*, 1944, [vii], 34, 828—833).—A discussion of the different ways of stating the second law of thermodynamics. Comments are made on a recent paper by Ehrenberg (A., 1943, I, 229). H. J. W.

Phase diagrams and the mass law. T. R. Briggs (*J. Chem. Educ.*, 1943, 20, 484—487, 510; A., 1924, ii, 836).—Mass law equations for calculating P - T - X phase diagrams for binary systems consisting of vapour and a congruently dissociating solid such as NH_4Cl or $\text{NH}_2\text{CO}_2\text{NH}_4$ are given. Diagrams for $\text{NH}_2\text{CO}_2\text{NH}_4$ in the system CO_2 - NH_3 at 10—50° and 0—400 mm. pressure are calc. L. S. T.

Statistics of binary systems (A) G. H. Wannier. (B) K. Fuchs (*Proc. Roy. Soc.*, 1943, A, 181, 409—411, 411—415).—(A) A criticism of the results obtained by Fuchs (A., 1942, I, 205).

(B) A reply.

G. D. P.

System hydrocyanic acid-diethyl ether.—See A., 1944, II, 71.

Vapour pressure data and phase diagrams for some concentrated soap-water systems above room temperature. J. W. McBain and W. W. Lee (*Oil and Soap*, 1943, 20, 17—25).—A series of isotherms have been constructed from v.p. data procured by the use of the McBain sorption balance for a typical commercial toilet soap and for pure Na laurate, myristate, palmitate, stearate, and oleate, and from this information the phase diagrams relating to the corresponding binary soap- H_2O systems have been revised and extended. The region of soap-boiler's neat soap in the soap- H_2O diagrams is shown to be a single homogeneous phase in all cases, its left-hand boundary agreeing with the T_c curve determined by other methods. The formation of the hemihydrates from curd is demonstrated in

the case of Na stearate, palmitate, and myristate: higher hydrates, e.g., Na palmitate, $9\text{H}_2\text{O}$, may exist at high R.H., as in the presence of isotropic solution. A photograph of "waxy soap" crystals growing from the "subwaxy" form as hydration progresses is given.

E. L.

Polytherm of the ternary system sodium bromide-potassium bromide-water from the temperature of complete freezing to 50° . N. A. Vlasov and A. G. Bergman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 148—151).—Ice, α -KBr, and $\text{NaBr}\cdot 5\text{H}_2\text{O}$ crystallise together at -32° and NaBr 36.5, KBr 4, H_2O 59.5 wt.-%. NaBr, $5\text{H}_2\text{O}$, NaBr, $2\text{H}_2\text{O}$, and α -KBr crystallise at -26° and NaBr 38, KBr 3.6, H_2O 58.4 wt.-%. NaBr, $2\text{H}_2\text{O}$, NaBr, and β -KBr crystallise at 46° and NaBr 47, KBr 7.8, H_2O 55.2 wt.-%. NaBr, $2\text{H}_2\text{O}$, α -KBr, and β -KBr crystallise at 7° and NaBr 41.4, KBr 5.4, H_2O 53.2 wt.-%.

J. J. B.

Distribution equilibria between molten metals and molten salts, with reference to the stability of intermetallic compounds in the molten state. E. Heymann, R. J. L. Martin, and M. F. R. Mulcahy (*J. Physical Chem.*, 1943, **47**, 473—484).—The distribution equilibria of Na between NaBr and Cd or Pb at 780° , and of Cd between CdCl_2 or CdBr_2 and Bi or Sb at 690° , have been investigated. The observed deviations from Raoult's law show that compounds between Na and Cd are decomposed at 780° and that intermetallic compounds between Na and Pb are stable in the liquid state at 780° . The curves for Cd- CdCl_2 (CdBr_2)-Bi are similar but both show anomalies in their max., suggesting that the curves do not truly represent the activity of Cd in the mixture. Sb is insol. in molten CdCl_2 in absence of Cd, but very sol. in presence of Cd, suggesting the formation of an intermetallic compound (CdSb ?) which is stable at 690° and very sol. in molten CdCl_2 .

C. R. H.

Equilibria of silver and lead, silver and bismuth, and bismuth and lead with their fluorides at 900° . H. H. G. Jellinek (*Trans. Faraday Soc.*, 1944, **40**, 1—5).—The equilibrium of Bi and Pb with their molten fluorides was determined at 900° in graphite vessels. Bi is by far the nobler in this reaction. The metal and salt phases are approx. ideal, and the calc. heat of formation of BiF_3 agrees with the accepted val. Similar determinations with Ag could not be carried out in open vessels owing to vaporisation of AgF , but equilibrium consts. for its reactions with PbF_2 and BiF_3 are estimated from the corresponding heats of reaction.

F. L. U.

The carbon-oxygen equilibrium in liquid iron. S. Marshall and J. Chipman (*Trans. Amer. Soc. Metals*, 1942, **30**, 695—746).—The equilibria between C and O in liquid Fe at 1540 — 1700° and CO and CO_2 in the surrounding gas at pressures >20 atm. were studied by the use of a closed high-frequency furnace. When equilibrium was reached, gas samples were withdrawn from the furnace for analysis and the steel was "killed" by the addition of Al and quickly cooled. The steel samples were analysed for [C] and [O], the latter being determined from the $[\text{Al}_2\text{O}_3]$. In the reactions, the equilibrium factors depend on [C]. The product of %C and %O in the metal is a function of temp., pressure, and [C]; at 1 atm. of CO + CO_2 at 1540° the val. varies from 0.0018 with 0.02% of C to 0.0034 with 1.0% of C. This effect is explained if $\sim 0.0028\%$ of CO is sol. as such in steel at 1540° under a pressure of 1 atm.

J. C. C.

Silicon-oxygen equilibria in liquid iron. C. A. Zapffe and C. E. Sims (*Amer. Inst. Min. Met. Eng.*, 1942, *Tech. Publ.* 1498, 30 pp.; *Metals Tech.*, **9**, No. 6).—The equilibria were studied by heating mixtures of Fe and Si in H_2 containing known amounts of H_2O , followed by quenching and chemical analysis. The equilibria could not be expressed in terms of $[\text{FeO}]$ and $[\text{Si}]$. Assuming the presence of SiO , the const. $K = [\text{FeO}][\text{Si}]$ agrees closely with theoretical vals. Free energy changes, heats of reaction, and entropy changes are calc. Total O in steel consists of FeO and suboxides of alloying elements and deoxidisers; if large amounts of the latter are present, determination of O by vac. fusion may give incorrect results.

R. KE.

VII.—ELECTROCHEMISTRY.

Nature of molten salts and their mixtures. M. F. R. Mulcahy and E. Heymann (*J. Physical Chem.*, 1943, **47**, 485—496).—Available data for the equiv. conductivity of molten alkali and alkaline-earth chlorides are applied to a discussion of the main factors governing the conductivity of molten salts. The conductivity of mixed molten salts and the non-additivity of conductivity where complex ion formation occurs are also discussed. N. W. Taylor criticises the theoretical treatment in this and in an earlier paper (Heymann *et al.*, *supra*).

C. R. H.

Transport numbers of nitric acid in water at 25° from e.m.f. measurements. H. I. Stonehill (*J.C.S.*, 1943, 647—651).—Since accurate activity coeff. data for HNO_3 are available (Hertmann *et al.*, *A.*, 1933, 675), transport nos. for HNO_3 can be obtained from the e.m.f. of cells with transport. The e.m.f. of a cell of the type $\text{Pt}|\text{quinhydrone (saturated)}|\text{HNO}_3 (m', \text{fixed})|\text{HNO}_3 (m, \text{variable})|\text{quinhydrone (saturated)}|\text{Pt}$ was determined, taking into account

the known salt error (Stonehill, *A.*, 1943, **I**, 130). Combining the results at different concns. (0.001—0.2M.) with activity coeff. data, the cation transport nos. (t_+) are calc. The results agree satisfactorily with the theoretical limiting val., and limiting slope of the t_+ -(concn.)¹ curve, and with the Jones-Dole equation (*A.*, 1929, 767) and the Longworth equation (*A.*, 1932, 914; 1935, 1078), but not with the Owen equation (*A.*, 1936, 292). Up to 0.2M. the mobilities of H^+ in HNO_3 and HCl of the same concn. are equal. The mobilities of NO_3^- in KNO_3 (up to 0.2M.) and in AgNO_3 (up to 0.1M.) are $<$ those in HNO_3 . KNO_3 and AgNO_3 are, therefore, incompletely dissociated at these concns.

A. J. M.

Electrostatic potentials in electrochemically important systems of rigid charge layers. E. Lange and M. Wiedemann (*Z. Elektrochem.*, 1941, **47**, 568—580).—The external and surface electrostatic potentials of certain systems of charge layers (spherical, circular disc, spherical condenser, plate condenser) are surveyed as functions of charge, dipole moment, and density. Potentials in systems of alternate layers of positive and negative charges, in systems of similarly charged layers, and for an adsorption layer with dipole structure on a metal base, are calc. The calculations are applied to ionic hydration, pyro- and piezo-electric crystals, and to metals in electrolyte solutions.

J. H. BA.

Over-potential of hydrogen in relation to the composition of the electrode material. U. Croatto and M. Da Via (*Gazzetta*, 1943, **73**, 117—133).—The over-potential (η) of H_2 was measured at 20° with varying c.d. in 6N-KOH with cathodes of binary alloys of Pb-Cd and Pb-Sb. In the eutectic ranges of the alloys the c.d. necessary to produce a given η varies linearly with the % composition of the electrode surface. In the regions of mixed crystals there is a rapid rise of η for Pb-Sb with increase of the lesser component, with a max. at the point where two phases are formed. The reverse is true for Pb-Cd. While two phases are present η rises gradually with increase of Cd or Sb. This can be explained by assuming that addition of Pb or Cd to each other increases the surface activity of the crystals by decreasing their stability, the reverse being assumed for the Pb-Sb alloy.

J. F. M.

Overpotential and corrosion. U. Croatto (*Gazzetta*, 1943, **73**, 133—143).—With Pb and its alloys with various metals (0.08 and 0.16%) as the cathode in 15N- H_2SO_4 at 120° the overpotential of H_2 at varying c.d., and the c.d. necessary to produce a given overpotential with various alloys, were measured. The results indicate that the corrosion of alloys of Pb with Ag, Ni, and Cu is electrochemical as well as chemical, but with Zn, Sn, Sb, Cd, and Bi is purely chemical.

J. F. M.

Electrophoretic properties of globin from various sources.—See *A.*, 1944, **III**, 138.

VIII.—REACTIONS.

Models of physico-chemical processes. G. K. Diakonov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 143—147).—Several dimensionless parameters are derived which determine the progress of physico-chemical reactions as Reynolds no. determines the kind of liquid flow. One of these parameters shows whether the reaction proceeds by a series of near-equilibrium stages, or takes place far from the equilibrium; another is the ratio between the time required for the completion of a reaction and the time available.

J. J. B.

Theory of the autogenesis of chain reactions. N. S. Akulov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 204—208).—It is assumed that the average length of the reaction chain does not change in the course of the reaction and is $=1/(k\delta - 1)$, δ being the probability of an active centre reacting with other mols., and k the no. of new centres created in this reaction. From these assumptions the main equations of chain processes, especially of explosion and flame reactions, are derived.

J. J. B.

Theory of combustion, ignition, and explosion. N. S. Akulov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **39**, 239—243).—From the equations obtained earlier (see preceding abstract) expressions are derived for the latent period of ignition and for the pressure-temp. dependence of the ignition limits including the "peninsula of ignition." The rate of reaction has a finite val. within the ignition limits and is 0 at the limits.

J. J. B.

Inflammability of methylene chloride-oxygen-nitrogen mixtures. G. W. Jones, R. E. Kennedy, and F. E. Scott (*U.S. Bur. Mines Rept. Invest.* 3727, 1943, 7 pp.).— CH_2Cl_2 - O_2 mixtures containing 15.5—66.4% of CH_2Cl_2 are inflammable. CH_2Cl_2 does not give inflammable mixtures with air at room temp. and pressure, but if the air is enriched to contain $<18.9\%$ of O_2 , inflammable mixtures are produced within certain limiting concns. of CH_2Cl_2 . CH_2Cl_2 vapour ignites in air at 642° and in O_2 at 606° .

J. W. S.

Unreleased energy in hydrocarbon flame gases. W. T. David and J. Mann (*Phil. Mag.*, 1944, [vii], **34**, 816—822).—Dry and moist hydrocarbon gases mixed with air in various proportions were burnt in an open burner and the flame temp. measured by the resistance of fine quartz-coated Pt-Rh wires. The unreleased

energy (latent energy abnormal dissociation) in the flame gases is calc. from the temp., sp. heat, and heat of combustion; as a function of the gas concn. in the mixture it first falls and then rises. The fall is due to a decrease in the latent energy, and the rise to abnormal dissociation. The effect of H_2O in dil. mixtures is to increase the flame temp. and decrease the unreleased energy; at higher gas concn. the moisture effects decrease to zero. H. J. W.

Mechanism of addition polymerisation. C. C. Price (*Ann. New York Acad. Sci.*, 1943, 44, 351—370).—Reactions which generate free radicals initiate many addition polymerisations, as indicated by the presence of fragments of them as end-groups in the resulting polymer. Analytical data are given for polystyrene and polymethyl methacrylate prepared in presence of acyl peroxides and diazohydroxides. The kinetics of the polymerisation of *d*-sec-Bu α -chloroacrylate catalysed by Bz_2O_2 are examined over the temp. range 26—88°, and a mechanism is allotted to it. Inhibitors may be free radicals which react with the active free radical interrupting the chain growth, or substances, e.g., aromatic NO_2 compounds, which increase the stability of radicals and so retard the polymerisation. Stabilisation of growing chains by chain transfer occurs in some cases. A mechanism involving an active cationoid intermediate, induced, e.g., by strong acids, BF_3 , $AlCl_3$, or $SnCl_4$, is operative in some polymerisations. This leads to different kinetics, which are examined for styrene polymerisation catalysed by $SnCl_4$.

R. H. F.

Kinetics and elementary steps of poly-reactions. J. Abere, G. Goldfinger, H. Mark, and H. Naidus (*Ann. New York Acad. Sci.*, 1943, 44, 267—296).—The course of poly-reactions may be followed by measuring the amount of monomer removed and the average degree of polymerisation and mol. size distribution of the polymer formed as a function of time and reaction conditions, and by chemical analysis of the polymer, and determination of the no. of active centres starting chains. Poly-reactions consisting of a single elementary step are of two types: (1) reaction occurs between monomers or polymers of any chain length (e.g., poly-esterifications), (2) only monomer addition takes place [e.g., addition of $(CH_3)_2O$ to glycols, amines, or acids]. Equations for rate of formation of polymer are derived for both cases. For poly-reactions consisting of initiation, propagation, and termination the possible mechanisms of each of these processes are examined. By equating the rate of formation and disappearance of active centres formulae are deduced for the rate of reaction and no. average degree of polymerisation of the polymer using all possible combinations of the mechanisms. In several cases experimental figures are compared with those calc. on probable assumptions, and appropriate mechanisms allotted. Formulae are deduced for the distribution curve of the polymer, and compared with experiment. Chain transfer and branching introduce additional complications. The activation, propagation, and termination processes are considered in detail.

R. H. F.

Kinetics of the oxidation of isopropyl alcohol by chromic acid. F. H. Westheimer and A. Novick (*J. Chem. Physics*, 1943, 11, 506—512).—The oxidation reaction is of the first order with respect to $[HCrO_4^-]$ and $[PrOH]$ and of the second order with respect to $[H^+]$. A compound of Cr^{IV} or Cr^V is concerned in the mechanism.

L. J. J.

Recent advances in the theory of reaction kinetics in solution. R. P. Bell (*J. C.S.*, 1943, 629—635).—Tilden lecture. A review of the theoretical explanation of velocities of bimol. reactions in solution is given. The collision theory and the transition state theory are discussed. The effect of interaction between solvent and solute is considered.

A. J. M.

Hydrolysis of acetyl and bromoacetyl bromides. J. Rodriguez Velasco and J. M. R. de La Borbolla (*Anal. fts. quim.*, 1943, 39, 31—36).—The velocity of hydrolysis of $AcBr$ and $CH_2BrCOBr$ is comparable with that of $AcCl$ and $CH_2ClCOCl$ (A., 1942, I, 369), although the coeffs. are higher. AcI and $CH_2I\cdot COI$ have analogous but higher coeffs. which are less precise owing to secondary reactions.

F. R. G.

Rate theory and some physical and chemical properties of high polymers. H. M. Hulbert, R. A. Harman, A. V. Tobolsky, and H. Eyring (*Ann. New York Acad. Sci.*, 1943, 44, 371—418).—The ionic and radical mechanisms of polymerisation are considered in relation to the electronic structure of the double bond. Initiation reactions are classified into (1) those with frequency factors of $\sim 10^{11}$ and activation energy ~ 40 kg.-cal. per mol., e.g., polymerisation of alkyl-substituted olefins catalysed by acids, $AlCl_3$, BF_3 , etc., (2) those with lower frequency factors and activation energies, e.g., styrene and acrylate polymerisations. The criteria of the ionic mechanism are change in rate on changing electronegativity of substituents, catalysis by acids or bases, and intramol. rearrangement during polymerisation. The kinetics of growth of chains by the ionic mechanism are worked out on the basis of polarisation of the double bond in its activated state. The kinetic data on polymerisation of vinyl compounds, especially styrene, are reviewed. Chain transfer, which terminates polymer mols. without interrupting the reaction chain, has a velocity ~ 0.001 of that of propagation. Formulae are derived for mol. wt. distribution and no.

average mol. wt., taking as a basis 8 general reactions of initiation, propagation, and termination, and considering the steady state with respect to no. of active mols. The distribution function agrees with data on styrene polymerised as pure liquid, after recalculation of mol. wts. A theory of physical properties of polymers in the rubber-like state of aggregation is developed, based on the no. of bonds per unit vol., strength of bonds, and internal viscosity of the local liquid-like structure. An equation of state derived from the relation between tension and entropy leads to a formula for the modulus of elasticity of rubber-like materials. Relaxation of stress, creep, and extrusion behaviour are accounted for by slipping of bonds, allowing chains to coil into random configuration. The motion of the mobile chain segments has a damping effect on mechanical properties. A formula is given for the most probable vol. of a randomly shaped chain, and a relation between η and mol. wt. is derived from it.

R. H. F.

Mechanism of inhibition of styrene polymerisation. G. Goldfinger, I. Skeist, and H. Mark (*J. Physical Chem.*, 1943, 47, 578—587).—Styrene polymerisation at 70°, 100°, and 130° is inhibited by benzoquinone (I), the length of the inhibition period being \propto initial concn. of (I). (I) is used up more rapidly at higher temp., indicating a considerable activation energy (27,000 g.-cal. per mol.) for the formation of the active centres which consume the inhibitor. After the induction period the overall rate of polymerisation and the no.-average degree of polymerisation of the polymer formed are inversely \propto initial concn. of (I).

C. R. H.

Spatial arrangement of atoms in contact catalysis and dehydrogenation of hydrocarbons with open chains. A. A. Balandin (*Acta Physicochim. U.R.S.S.*, 1943, 18, 69—90).—The multiplet theory of catalysis, in which the shape and size of mols. and of the lattice of the catalyst are regarded as of primary importance, is discussed with particular reference to the dehydrogenation of hydrocarbons. Models indicating the orientation of $n-C_4H_{10}$ (I), Δ^a -butene (II), and PhEt mols. when undergoing catalytic dehydrogenation are drawn, and the reactions are studied, using the flow method. With (I), the dehydrogenation at a Cr_2O_3 catalyst amounts to 52% of (I) passed, or to 85% of that decomposed at 570°, and a spatial velocity of 700—1000 l. per hr. At lower temp. the yield on the basis of (I) passed decreases, whilst that based on (I) decomposed increases. The yield-time of contact (*t*) curves, drawn for various temp., show a max., indicating an optimum *t*. The composition of the contact gas at 570° and *t* = 1.5 sec. is H_2 37.5%, CH_4 2.4%, C_2H_6 3.7%, C_2H_4 0.3%, C_3H_8 0.1%, C_4H_8 29%, C_4H_{10} 26.8%. The dehydrogenation and formation of C compete with one another on Cr_2O_3 catalysts, and the Cr_2O_3 becomes deactivated owing to C films, but is readily regenerated. With (II), activity decreases above a certain temp., probably owing to decomp. of products. The yield of butadiene at 600° is 34% based on (II) passed and 75% based on (II) decomposed. The most important side-reaction is $C_4H_8 + 4CO_2 = 8CO + 4H_2$, but the CO does not poison the catalyst. The activity varies with time in a peculiar manner. The dehydrogenation of (II) has also been investigated at low pressures, in which case the optimum *t* is greater. The effect of dilution with CO_2 and N_2 was also studied. Two methods for the production of styrene (III) from PhEt are given. There is again an optimum *t*. The effect of addition of (III), PhMe, and C_6H_6 , respectively, to PhEt undergoing dehydrogenation indicates the following sequence of mean lives of mols. on the active surface: (III) > PhEt > PhMe > C_6H_6 . The curves of yield of (III) against *t* are similar to those obtained in the pyrolysis of PhEt.

A. J. M.

Isotherm of heterogeneous catalytic reactions carried out under flow method conditions and a new method for determining the relative adsorption coefficients. A. L. Liberman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 448—452).—An equation connecting reaction velocity with adsorption on reaction centres, which is based on Langmuir's equation and also takes into account the change in vol. occurring during a reaction, has been derived. This equation, $m/M = 2k/\beta m - 2/\beta$ (*M* and *m* are respectively the no. of mols. of reactant entering the reaction tube and the no. of such mols. reacting per unit time, $\beta = a_2/a_1 + a_3/a_1$, where a_1 , a_2 , and a_3 are the adsorption coeffs. of reactant and reaction products, and *k* is a reaction rate coeff.), has been satisfactorily applied to data for the dehydrogenation of *sec*-BuOH, for which reaction $\beta = 7.4$.

C. R. H.

[Oxidation of ammonia.] N. S. Bayliss (*J. Chem. Educ.*, 1943, 20, 510).—A heated helix of Pt wire is used as catalyst.

L. S. T.

Cracking of cyclohexane: thermal and catalytic decomposition at high pressures.—See B., 1944, II, 1.

Catalytic desulphurisation of gasolines by cobalt molybdate.—See B., 1944, I, 46.

Organic catalysts for the elimination of carbon monoxide from formamide. II. Catalysts with phenol hydroxyl at active group.—See A., 1944, II, 70.

Electrolysis with undulating current. II. Production of ozone by electrolysis. E. Briner and A. Yalda (*Helv. Chim. Acta*, 1943, 26,

1162—1166; cf. A., 1943, I, 232).—When an increasing intensity of a.c. is superposed on d.c. the yield of O_3 increases to a max. and then falls to zero. F. J. G.

Production of hydrogen and oxygen by electrolysis of water.—See B., 1944, I, 53.

Iron plating.—See B., 1944, I, 69, 70.

Electrodeposition of cobalt-tungsten alloys from an acid plating bath.—See B., 1944, I, 72.

Continuous plating of fine steel wire with nickel.—See B., 1944, I, 70.

Electrofinning.—See B., 1944, I, 71.

Darkening of cadmium halides and of antimony oxide by ultra-violet light. G. Cohn and J. A. Hedvall (*J. Physical Chem.*, 1943, 47, 603—607).—The photosensitivity of crystals of CdI_2 , $CdBr_2$, and Sb_2O_3 towards ultra-violet light depends on crystallographic factors, occurring either at strongly absorbing crystal faces or in presence of an unstable modification. Darkening of the crystals only occurred in presence of H_2O , and a photosensitised reaction mechanism involving H_2O and leading to the formation of Cd or Sb is proposed. C. R. H.

Kinetics of photographic development by hydroxylamine. T. H. James (*J. Physical Chem.*, 1943, 47, 597—602).—In the development of AgBr film with NH_2OH at 20° the relation between Ag formed and optical density (D) can be expressed by $\log Ag = 1.42 \log D + \text{const.}$, this being approx. the same relation as found for development by quinol. The rate of development increases regularly with pH over the pH range 10—12.7 and with $[NH_2OH]$ and decreases with increase in $[Br^-]$. Small amounts of Na_2SO_3 affect the rate of development only slightly, but large amounts decrease the rate and in extreme cases shift the character of development to the so-called "physical" type. Fog formation is primarily due to an uncatalysed reaction. The data support the view that development is a catalysed heterogeneous process which takes place preferentially at the interface between Ag and Ag halide. C. R. H.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Isotope separation and the mechanism of combustion in ascending hydrogen-deuterium flames. K. Clusius, W. Kölsch, and L. Waldmann (*Z. Elektrochem.*, 1941, 47, 820).—In ascending H_2 - D_2 - O_2 flames, a slight separation of isotopes occurs on account of partial combustion. H_2 is enriched in the H_2O , and D_2 in the unburnt gas. A. J. M.

Regeneration of acid cuprous chloride solution. G. E. Mapstone (*J. Proc. Austral. Chem. Inst.*, 1943, 10, 267—268).—Regeneration of spent Cu_2Cl_2 solution (oxidised during the process of CO gas analysis) is effected by placing the solution, with HCl, in a bottle containing Cu wire extending from top to bottom. Reduction is complete in 2—3 days. R. H. H.

Hydration of the aluminates of calcium. V. Hydrothermal decomposition products of tricalcium aluminate at 350° . H. Johnson and T. Thorvaldson (*Canad. J. Res.*, 1943, 21, B, 236—246).— $Ca_3Al_2O_6$ or the corresponding mixture of CaO and Al_2O_3 yields a cryst. product (I) $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ (n 1.627, d^{20} 2.71) and $Ca(OH)_2$ when treated with steam at 350° . (I) dehydrates between 650° and 750° in dry air to give $12CaO \cdot 7Al_2O_3$ and Al_2O_3 . X-Ray powder patterns of (I) and its dehydration products are given. J. H. Ba.

Complexes of zinc and glycine. I. Greenwald (*J. Physical Chem.*, 1943, 47, 607—622).—pH and titration data for mixtures of glycine and ZnCl₂ indicate the existence in solution of ZnX^{++} , $ZnXOH^+$, $ZnX(OH)_2$, $ZnX_2O_2H^+$, and $ZnX_3O_2^{++}$ where $X = O_2C \cdot CH_2 \cdot NH_2$. Vals. for the consts. for the formation of the first four complexes have been calc. The following compounds have been cryst.: $Zn(HO_2C \cdot CH_2 \cdot NH_2)_2 \cdot Cl_2 \cdot H_2O$; $ZnXCl_2 \cdot H_2O$; $ZnX_3(OH)(ONa) \cdot H_2O$; $ZnX_4(ONa)_2 \cdot H_2O$. No satisfactory evidence for the existence in solution of the complex cation of the first compound, i.e., $Zn(HO_2C \cdot CH_2 \cdot NH_2)_2^{++}$, has been obtained. C. R. H.

Co-precipitation of cadmium and mercuric sulphides. E. S. Rittner and J. H. Schulman (*J. Physical Chem.*, 1943, 47, 537—543).—Cubic CdS changes to the hexagonal form if kept in contact with a conc. solution of $(NH_4)_2S$ for two days at room temp., or with 0.3N- HNO_3 at 100° for a week. Heating CdS at 500° for a week or at 700 — 900° for a few min. and then rapidly cooling brings about the same change. The vac. sublimation of HgS (red cinnabar) on to a cooled glass surface yields a new form of cinnabar which is black. CdS-HgS solid solutions, which are formed at room temp. by direct reaction of stable or unstable CdS and HgS in contact with conc. $(NH_4)_2S$, exist in cubic or hexagonal CdS form but not in hexagonal HgS form. The presence of CdS inhibits and may prevent the transformation of metacinnabar into cinnabar when Cd and Hg are co-pptd. in presence of $(NH_4)_2S$. When co-pptd. in presence of 0.3N- HNO_3 solid solutions of the metacinnabar type

are formed from nitrate and chloride solutions, cubic structures also being formed in chloride solutions. C. R. H.

Over-compression of mercury fulminate. K. K. Andreev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 456—458).—Published work on the influence of high pressures on the detonation of Hg fulminate is discussed with reference to the mechanism of detonation. C. R. H.

Peroxytitanates. J. Beltrán (*Anal. fis. quim.*, 1943, 39, 373—381).— $Na_4TiO_6 \cdot 2 \cdot 4H_2O$ contains 4 atoms of active O of which only 2 are peroxide O, whence the formula $Na_4TiO_6 \cdot 2H_2O_2$ is suggested. F. R. G.

Co-ordination number of bivalent lead. R. C. Haworth and F. G. Mann (*J.C.S.*, 1943, 661).—The compound $6CS(NH_2)_2 \cdot Pb(NO_3)_2$, m.p. 160° (decomp.), undergoes considerable dissociation in boiling dil. aq. solution, but crystallises unchanged on cooling. If the 6 mols. of $CS(NH_2)_2$ are co-ordinated normally to Pb, giving the salt $[(CS(NH_2)_2)_6Pb](NO_3)_2$, the Pb has the electronic state of U. The compound may, however, be a mol. additive compound. A. J. H.

Plastic sulphur. M. Epstein (*J. Chem. Educ.*, 1943, 20, 360).—A hot test-tube containing boiling S is plunged into cold H_2O . When cold, the shattered tube can be stretched. L. S. T.

Decomposition of sulphur monoxide and the polysulphur oxides. P. W. Schenk (*Z. Elektrochem.*, 1941, 47, 855).—Both SO, condensed by liquid air, and its decomp. products contain SO groups, since both react with Cl_2 giving $SOCl_2$. If condensed SO is mixed with cooled CCl_4 or certain other solvents intensely yellow solutions are produced, and after removing the solvent, a yellow plastic substance remains which has the same reactions as SO obtained by warming the condensate. The mol. wt. of SO dissolved in CCl_4 is ~ 800 . The condensed SO and its decomp. product are regarded as high-mol. poly-S oxides of variable composition. A. J. M.

Conductometric elucidation of complex chromium cations. III. Masking action of monobasic organic acids. S. G. Shuttleworth (*Leather Ind. Res. Bull. [S.A.]*, 1943, 2, Circ. 24, 357—365).—From conductometric titration curves of acetate, acetato-sulphate, formato-sulphate, and levulinato-chromium complexes it is shown that the Na salts of monobasic org. acids displace the SO_4 groups in a sulphato-Cr complex, forming a new complex containing no electrovalent groups. It reacts with dil. alkali to form a 66.67% basic Cr complex which is fully elated, the stability of which varies inversely as the strength of the acidic group therein. A structural explanation is offered. D. W.

Peroxyuranates. J. Beltrán (*Anal. fis. quim.*, 1943, 39, 368—372).— $Na_4UO_6 \cdot 8H_2O$ does not lose its 3 atoms of active O on drying at 100° . 2 atoms are instantaneously hydrolysed in H_2O or alkaline solution. It is concluded that H_4UO_6 is a true peroxyacid. F. R. G.

Safe handling and storage of anhydrous hydrofluoric acid.—See B., 1944, I, 52.

Behaviour of ferric oxide towards added foreign oxides at temperatures about 1300° . N. G. Schmahl (*Z. Elektrochem.*, 1941, 47, 835—843).—By direct isothermal determinations of O_2 pressure, the effects of BeO , Al_2O_3 , Cr_2O_3 , Mn_2O_3 , SiO_2 , and TiO_2 on the equilibrium $6Fe_2O_3 \rightleftharpoons 4Fe_3O_4 + O_2$ have been investigated, the temp. being usually 1323° (in a few cases 1060°). Isothermal concn.-pressure diagrams are constructed. BeO , Al_2O_3 , and SiO_2 exert very little effect. Cr_2O_3 and TiO_2 form very stable solid solutions with the Fe oxides, and therefore exert a marked effect on the equilibrium. TiO_2 forms Fe^{III} titanates with the Fe_2O_3 . In the case of Mn_2O_3 , the Fe_2O_3 acts as the foreign oxide, reducing the Mn_2O_3 to MnO , and forming a spinel, $MnO \cdot Fe_2O_3$. A. J. M.

Constitution of sodium nitroprusside. F. E. Raurich S. (*Anal. fis. quim.*, 1943, 39, 55—132).—Comparison of the properties of $Fe(NO)(CN)_5$ with those of metallic cyanides indicates that the metal is Fe^{II} . F. R. G.

Application of artificial radioelements to the elucidation of problems of chemical complexes. A. A. Grinberg and P. M. Filinov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 31, 453—455).—Using radioactive Pt and Ir it has been shown that there is no exchange of central ion between $[PtCl_6]^{--}$ and $[Pt(NH_3)_4Cl_2]$, $[IrCl_6]^{--}$ and $[IrC_2H_5N_3Cl_4]$, and $[IrCl_6]^{--}$ and $[Ir(C_2H_5N)_3Cl_3]$. The considerable difference in the activities of Pt and Ir after bombardment with neutrons suggests a simple method of determining traces of Ir in Pt. C. R. H.

X.—LECTURE EXPERIMENTS AND HISTORICAL.

Calorimetric studies of various types. D. B. Pattison, J. G. Miller, and W. W. Lucasse (*J. Chem. Educ.*, 1943, 20, 319—326).—The following reactions, suitable for calorimetric measurements, are described: the decomp. of H_2O_2 , the reaction of CaC_2 with aq. HCl, of aq. $Hg(NO_3)_2$ with aq. NaCl, of aq. $CuSO_4$ with aq. NH_3 , of aq. $KBrO_3$ with aq. HBr, of aq. $MgSO_4$ and aq. $Al_2(SO_4)_3$ with

aq. NaOH, of Ac_2O with aq. NaOH, and of NH_4OH and COMe , the dissolution of anhyd. and hydrated NaOAc , and the heat of dilution of EtOH by H_2O . L. S. T.

Chemical knowledge in the Old Testament. S. Isserow and H. Zahnd (*J. Chem. Educ.*, 1943, 20, 327—335). L. S. T.

Rise and development of chemistry in the Argentine Republic. V. Arreguine (*J. Chem. Educ.*, 1943, 20, 474—478). L. S. T.

Chapter of the history of chemistry in Vienna. Adolf Lieben, 1836—1914; Zdenko Hans Skraup, 1850—1910. M. Kohn (*J. Chem. Educ.*, 1943, 20, 471—473). L. S. T.

James Curtis Booth, chemist, 1810—1888. E. F. Smith (*J. Chem. Educ.*, 1943, 20, 315—319, 357). L. S. T.

Selected references to biographical sketches of 100 well-known chemists. G. L. Fraser (*J. Chem. Educ.*, 1943, 20, 506—507). L. S. T.

XIII.—GEOCHEMISTRY.

Hydrochemical features of the rivers Dubna, Sestra, Jachroma, Ikscha, and Volguscha in 1932—1933. B. A. Skopintzev and S. M. Dratshev (*Hydrochem. Mat.*, 1941, 12, 155—157).—The above rivers are tributaries of Upper Volga. J. J. B.

Hydrochemical behaviour of the river Volga and some rivers of the Volga basin in winter under ice. B. A. Skopintzev (*Hydrochem. Mat.*, 1941, 12, 159—168).—The $[\text{O}_2]$ of the river H_2O decreases during the winter to a min. in March or April since in the winter months the rivers are fed with deep ground H_2O containing but little air. J. J. B.

Hydrochemical sketch of the river Piasina. V. S. Ivlev (*Hydrochem. Mat.*, 1941, 12, 169—181).—The river is in the Siberian tundra. J. J. B.

Hydrochemical features of the river Volga between Kalinin and the river Dubna in 1931—1934. S. M. Dratshev and B. A. Skopintzev (*Hydrochem. Mat.*, 1941, 12, 151—154). J. J. B.

Volumetric zinc uranyl determination of sodium by the method of Dobbins and Byrd. N. Veselovski (*Hydrochem. Mat.*, 1941, 12, 25—33).— $[\text{Na}]$ of 11 samples of ground H_2O of Lower Don district is given (cf. C., 1944, Part 1). J. J. B.

Determination of sulphates in water and in aqueous extracts from soil and medicinal mud by titration of the excess of barium chloride with potassium chromate in presence of rosolic acid. M. Konarev (*Hydrochem. Mat.*, 1941, 12, 79—85).— $[\text{SO}_4]$ of 18 water samples from the Lower Don district are given (cf. C., 1944, Part 1). J. J. B.

Determination of sulphates in water and aqueous extracts from soil and medicinal mud by titration in presence of sodium rhodizinate. M. Konarev (*Hydrochem. Mat.*, 1941, 12, 87—102).— $[\text{SO}_4]$ of 29 samples of water from the Lower Don district are given (cf. C., 1944, Part 1). J. J. B.

Volumetric benzidine method of determining sulphates in water and in aqueous extracts from soil and medicinal mud. M. Konarev (*Hydrochem. Mat.*, 1941, 12, 103—117).— $[\text{SO}_4]$ of 17 H_2O specimens from the Lower Don district are determined (cf. C., 1944, Part 1). J. J. B.

Radioactivity of the waters and rocks of Matzesta. M. S. Merkulova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 347—349).—Analyses are given. A. J. M.

Determination of the age of the waters of Matzesta. M. S. Merkulova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 459—460).—The calculation of the age of the waters of Matzesta from the He/A ratio according to the method of Savtschenko gives 2.02×10^8 years. C. R. H.

Geochemistry of subterranean waters of Tartar Republic. N. V. Tageeva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 244—247).—Petroleum usually is associated with waters containing much Ca , Cl , B , Sr , Ra , Br , and I , and a subnormal amount of SO_4 . Waters from the carboniferous strata of Tartar Republic belong to this group. J. J. B.

Characteristics of ice from the Kungur cave. G. A. Maximovitsch and G. G. Kobjak (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 478—481).—The physical and chemical properties of ice taken from various parts of the Kungur cave in the Urals are tabulated. C. R. H.

Radiogenic heat in rocks. N. B. Keevil (*J. Geol.*, 1943, 51, 287—300).—Several hundred new radioactivity determinations are combined with earlier data, and presented as frequency-distribution curves for granitic, other acidic, intermediate, basaltic, ultra-basaltic, and sedimentary rocks, and soils and clays. The data lead to probable rates of heat production lower than those estimated previously. This may be due partly to non-representative sampling. Analyses for Ra alone are not satisfactory. When a $\text{Th}:\text{U}$ ratio of 3.5, the average abundance ratio in rocks, is assumed, the rate of heat production is $H = 2.15a + 0.05K$ g.-cal. per g. per 10^6 years,

where a is the no. of α -rays emitted per g. per hr. and K the wt.-% of K . K/a can be assumed to be 2.06, so that $H = 2.25a$. The data show that the errors in using this simple method are negligible. L. S. T.

Statistical investigation of rounded Ural diamonds. I. I. Schrafanovski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 791—793).—The const. of diamonds from a no. of Ural districts are given. A. J. M.

Solution etching of detrital staurolite. G. Bond (*Geol. Mag.*, 1943, 80, 155—156).—Etching of staurolite grains by a solution from overlying basalt is described. L. S. T.

Fluorite and other minerals in Lower Permian rocks of S. Durham. A. Fowler (*Geol. Mag.*, 1943, 80, 41—51).—Occurrences of fluorite (I) and barytes (II) as cavity fillings in the magnesian limestone of S. Durham are described. (II) is present in relatively small amount, and is seldom associated with (I). Origin and order of deposition of these and associated minerals are described. L. S. T.

Mineralisation of Permian rocks of S. Durham. T. S. Westoll (*Geol. Mag.*, 1943, 80, 119—120; cf. preceding abstract).—Primary deposition of the ores may have been due to the presence of decaying macerated org. tissues, possibly with the help of S-bacteria. L. S. T.

Regeneration in rocks. J. S. Visnevski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 797—798).—The occurrence of desericitisation of plagioclase is described as an example of regeneration of rocks. A. J. M.

Age of Lovozero tundras. E. K. Gerling, L. V. Komlev, K. N. Sokolova, and V. G. Barkan (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 135—136).—Determinations by the He method using loparite and a loparite concentrate give an age of $231-266 \times 10^6$ years, and indicate that the Lovozero massif was formed in the same epoch as the Chibiny massif, and was complete not later than the Lower Carboniferous. L. S. T.

Stratification and a law of sedimentation of clastic deposits. V. P. Baturin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 137—140).—Theoretical. L. S. T.

Cambrian carbonate deposits of the Ussin-Tomsk watershed of the Kuznetsk Alatau. A. L. Dodin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 143—144).—Palaeontological evidence establishes the age of the marmorised limestones as Middle Cambrian. The Mn mineralisations associated with the carbonate deposits of the Ivanov and Isras mines are described. L. S. T.

Age of Africanda pyroxenite intrusion of the Kola Peninsula. E. K. Gerling, L. V. Komlev, V. G. Barkan, and M. E. Ermolaeva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 769—770).—The age calc. by the He method for knopite from the pyroxenite intrusion is $358 (? 385) \times 10^6$ years. That of knopite from a nepheline vein was calc. to be 249×10^6 years, but this is regarded as an underestimate. A. J. M.

Amphibole of variable composition from the region of the Cheliabinsk granite massif. M. E. Jakovleva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 794—796).—Analyses and optical properties of amphiboles of different colours are given. Increase of $[\text{Fe}_2\text{O}_3 + \text{FeO}]$ results in increase of n and decrease of optic angles. The angle of extinction is unaltered and the birefringence slightly reduced. The vals. of the optical const. have been used to determine the $[\text{Fe}_2\text{O}_3 + \text{FeO}]$ of other specimens of amphibole. A. J. M.

Products of fusing hornblende with fluoride additions. D. P. Grigoriev and O. N. Lebedeva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 787—790).—A 9:1 mixture of hornblende and NH_4F was fused. The melt contained mica of the phlogopite type, amphibole (I), magnetite (II), and an unknown mineral, identified by analysis as Ca silicofluoride (III). The order of separation is (II), mica, (I), and (III). The order of separation of (I) and mica is discussed. The intergrowth of the two crystals indicates the existence of epitaxy, which may be due to the structural similarity of the two minerals. A. J. M.

Celestite in the Permian deposits of the Bashkir Autonomous Socialist Soviet Republic. V. P. Florenski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 784—786).—The characteristics of celestite from this region are outlined, and its origin is discussed. A. J. M.

Calcite in the decomposed tectonic zones of the Chibiny tundras. B. N. Melentiev, P. K. Semenov, and P. N. Tschirvinski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 782—783).—Analysis of calcite veins from this district is given. The mineral is found in association with aggregates of optically negative chabasite. A. J. M.

Effect of oxidation on magnetic properties of magnetite. O. N. Althauzen (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 566—568).—The effect of heating in air on the magnetic properties of artificial and natural magnetite has been investigated. There is no simple connexion between Fe_2O_3 content and . A. J. M.

Natural residual magnetism of rocks. T. Roze (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 31, 662—670).—The effect of cooling

from above the Curie point on rocks in a magnetic field has been investigated. Data obtained support the hypothesis that the natural residual magnetisation of rocks is due to their cooling in the terrestrial field. W. R. A.

Irreversible variation of the magnetic properties of magnetites. O. N. Althauzen (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 661—664).—The irreversible changes in coercive force and max. susceptibility of magnetites from Wyssokaja, Magnitnaja, Tejskoye, and the Kola Peninsula on heat-treatment have been investigated. The influence on the terrestrial field of variation in temp. of the rocks of magnetite-bearing localities is discussed. W. R. A.

Mineralogy of the Urutukan deposit (Upper Kolyma, Far East Region). G. P. Barsanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 689—690).—Specimens from the Urutukan deposit are pieces of a quartz-sulphide vein—have been examined and a genetic scheme is tentatively advanced. W. R. A.

Diagram showing the dependence of coloration of magnesian-ferrous micas on the content of iron oxides. D. P. Grigoriev and A. V. Kotulski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 691—693). W. R. A.

Talc-magnesite and quartz-magnesite rock, Cobb-Takaka district. H. W. Wellman (*New Zealand J. Sci. Tech.*, 1942, **24**, B, 103—127).—Deposits of magnesite (I) rock in the upper basin of Takaka River are described and estimated quantities given. Chemical analyses recorded show the presence of 40—80% of (I) with almost complete absence of CaO. Analyses showing the progressive alteration of serpentine to (I) rock are also recorded and discussed. A ternary diagram showing the range in mineral composition of talc-magnesites is given. Economic possibilities and uses of the deposits are discussed. L. S. T.

Cuspidine and villiaumite in welding slag. V. V. Lapin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 694—696).—Artificial cuspidine has been prepared pyrogenetically in a welding slag. Small quantities of CaF₂, perovskite, villiaumite, and chromospinel are simultaneously formed. W. R. A.

Problem of the occurrence of beach-limestone at [Brown's Island] Auckland, New Zealand. J. A. Bartrum (*New Zealand J. Sci. Tech.*, 1942, **23**, B, 92—96).—The beach-limestone is not comparable with that of tropical regions, but is the product of special local conditions. Restricted ground-H₂O circulation may have dissolved CaCO₃ from shell material to saturation point, after which pptn. was initiated by causes unknown. L. S. T.

Rosasite from Kyzyl-Espse deposit. N. G. Sumin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 779—781).—The consts. (optic angle, dispersion, n , and hardness) of rosasite from this region are given. The chief component oxides are CuO, ZnO, CO₂, and H₂O, but the quantity of mineral available was insufficient for complete analysis. A. J. M.

Change of colour and optical properties of beryls on heating. B. A. Gavrusevitch and F. J. Sarapulov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 775—778).—Coloration, transparency, and vitreous lustre of beryls decrease suddenly as temp. is increased above 600°. n and birefringence also decrease somewhat. A. J. M.

New luminescence method for establishing the bituminous nature of rocks. V. N. Florovskaja (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 359—360).—The ultra-violet luminescence of a no. of minerals containing bitumen has been investigated, and the method is suggested for the detection of bitumen in rocks. A. J. M.

Micaceous kimberlites in the north of Central Siberia. G. Moor (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 363—365).—Analysis of rock from the Upper Taimyra river shows that it closely resembles the micaceous kimberlites of S. Africa. In the northern parts of Central Siberia rocks of both the micaceous kimberlite and the basalt kimberlite types are found. It is possible that diamonds may occur in Central Siberia. A. J. M.

Silver-bearing tetrahedrite from Nagolnaya Tarasovka in the Donetz Basin. E. K. Lazarenko (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 475—477).—The composition of the Ag-bearing tetrahedrite at Zhuravka (Nagolnaya Tarasovka) can be approx. expressed by (Sb,As)₂S₃·3—8(Cu₂Ag₂FeZnHg)S. It has $d^{17\pm}$ 4.889. C. R. H.

Vallerite from vein deposits of sulphide copper-nickel ores of the Monche-Tundra. I. N. Tschirkov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 472—474).—Vallerite occurs infrequently in ores of the Monche-Tundra generally associated with cubanite, both minerals having been formed, apparently, at the same time. C. R. H.

Ishkulite. New mineral of the spinel group. G. P. Barsanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 468—471).—Ishkulite, found in the northern part of the Ilmen reserve, is a hard, highly magnetic ore of d 5.0791, the physical properties being similar to

those of magnetite. Its formula is FeO.(Fe,Cr)₂O₃ with a portion of FeO isomorphously replaced by MgO. C. R. H.

Luminescence method for detecting uranium minerals and ores. U. G. Melkov and Z. M. Sverdlov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **31**, 361—362).—To obtain luminescent compounds from U-black, nasturan, and other ordinarily non-luminescent U ores, the minerals are sprayed with H₂SO₄, HNO₃, HCl, AcOH, or H₃PO₄. They then show luminescence when irradiated with short- λ ultra-violet. The method can be used for detecting U minerals. A. J. M.

Pre-anorthosite granite of the Grenville sub-province Quebec. C. Faessler (*Natural. Canad.*, 1943, **70**, 97—138).—Recent opinions on the existence of a granite older than the Morin anorthosite are reviewed. L. S. T.

Crystal structure of braunite, 3Mn₂O₃·MnSiO₃. A. Byström and B. Mason (*Arkiv Kemi, Min., Geol.*, 1943, **16**, B, No. 15, 8 pp.).—Braunite from various sources has a body-centred lattice with a 9.41, c 18.7 Å. The determination of the space-group is discussed. D_{10}^{25} —14c2 gives an approx. correct distribution of O. A. J. M.

Orthopyroxene from Dodkanya, Mysore. P. R. J. Naidu (*Current Sci.*, 1943, **12**, 253—255).—The mineral occurs in grains up to 1 cm. in length in a norite of the gneissic complex. Full data for the cryst. and optical properties and for the chemical composition are reported. The analysis points to the bushveldt rather than the charnockite type. N. M. B.

Copper deposits of Australia. A. B. Edwards (*Proc. Austral. Inst. Min. Met.*, 1943, No. 130, 105—171).—The Cu deposits of numerous localities and mines are described. Chemical analyses of two feldspar porphyrys from Moonta, and of ekmanite from Great Cobar mine, are recorded. L. S. T.

Natural mineral amalgams. D. R. Hudson (*Metallurgia*, 1943, **29**, 53—60).—Native Ag amalgams occur as mercurial Ag, a grey-white ductile mineral of variable composition containing >55% Hg in solid solution in the Ag lattice, or as argentiferous lundbergite, the brittle intermetallic compound Ag₃Hg₄, crystals of which are usually coated with free Hg. The occurrence, properties, and crystal habits of these minerals are critically reviewed. Brief reference is made to native amalgams of Pb, Pd, and Au. J. C. C.

Identification of clay minerals in some Iowa and New England soil profiles. J. L. Haddock (*Iowa State Coll. J. Sci.*, 1943, **18**, 42—44).—Clay minerals in 5 Iowa and 5 New England soils were determined by integrating data from thermal analysis, base-exchange capacity, and non-exchangeable K determination. F. R. G.

X-Ray analysis of Spanish clays. A. Hoyos (*Anal. fis. quim.*, 1943, **39**, 351—367).—In 68 clays examined from a no. of localities, moscovite, quartz feldspar, and CaCO₃ were identified. F. R. G.

Anomalous heat adsorption of kaolinite. F. H. Norton and W. G. Lawrence (*J. Amer. Ceram. Soc.*, 1943, **26**, 388—389).—The 2- μ . monodisperse fraction of Florida kaolin required 50% more heat to drive off the H₂O of crystallisation than did pure kaolinite. In absence of other plausible explanations of this anomaly, the existence of two forms of kaolinite is postulated. J. A. S.

Filtration stratification of highly disperse weathering and humification products in the profile of medium developed brown clay. H. Pallmann, E. Frei, and H. Hamdi (*Kolloid-Z.*, 1943, **103**, 111—119).—Processes involved in soil formation, and production of the various types of stratification, are considered. Filtration stratification is the most important, and the layers comprise SiO₂-Fe₂O₃ complexes of very variable composition. The Fe and Al silicates appear to act as stabilisers. A more or less thick protective skin of SiO₂ is formed around the clay nuclei, and is dissolved or dispersed by solutions of oxalates. A. J. M.

Forms of inorganic phosphorus in the lower horizons of some Iowa soils as indicated by plant availability and chemical methods. M. Stelly (*Iowa State Coll. J. Sci.*, 1943, **18**, 89—91).—Fertility of sub-soils is considered to depend on their content of acid-sol. P. F. R. G.

X-Ray study of soils in São Paulo state. J. E. de Paiva Netto (*Rev. Brasil. Quim.*, 1943, **16**, 99—113).—79 samples have been examined for the constituents of the clay minerals, and the location of these is recorded. F. R. G.

Colloid chemistry of soil types of Asia Minor. R. Lorenz (*Kolloid-Z.*, 1943, **103**, 171—180).—Climatic and vegetation zones in Asia Minor are reviewed as regards their effect on the soil. The various types of soil in different parts of the country are described, and the part played by the unfavourable distribution of H₂O is discussed. A. J. M.

Bird's-eye coal from Greymouth, New Zealand. M. Gage and J. A. Bartrum (*J. Geol.*, 1943, **51**, 320—329).—Examples of eye-structure in early Tertiary bituminous coal are described. Photographs are reproduced, and origin is discussed. L. S. T.

A I—General, Physical, and Inorganic Chemistry.

APRIL, 1944.

I.—SUB-ATOMICS.

Photo-excitation in hydrogen and deuterium by caesium ions of 2500—25,000 e.v. K. Mehnert (*Z. Physik*, 1941, 117, 41—54).—Excitation functions for collisions between Cs^+ and H_2 and D_2 have been measured for a no. of H and Cs^+ lines in the energy interval 2500—25,000 e.v., at low gas pressures and rates of ionisation. Stronger excitation of both Cs^+ and H lines is produced by $\text{Cs}^+ \rightarrow \text{D}_2$ than by $\text{Cs}^+ \rightarrow \text{H}_2$. For small kinetic energies, equal excitation of H_2 , D_2 , and Cs^+ lines is produced in collisions involving H_2 or D_2 mols. of equal kinetic energy, if the Cs^+ is considered as stationary. For higher energy, H_2 produced the greater excitation. If the centre of gravity of the collision partners is considered as stationary, excitation depends only on their kinetic energy. At high energies, greater excitation is produced in H_2 . L. J. J.

Exchange of charge with simultaneous excitation in collisions of alkali-metal ions with hydrogen, helium, and mercury. K. Mehnert and W. Maurer (*Z. Physik*, 1941, 117, 55—63).—Alkali-metal arc lines emitted in collisions of alkali-metal ions with H_2 , D_2 , He, and Hg are due to exchange of charge between the collision partners with simultaneous excitation of the alkali-metal atom formed. The lines emitted show the Doppler effect expected. Their intensity increases linearly with the gas pressure. The resonance principle is complied with. Excitation functions of $\text{Cs } 3^2P_{3/2} \rightarrow 1^2S_{1/2}$ ($\lambda 4555 \text{ \AA}$) in $\text{Cs}^+ \rightarrow \text{H}_2$ and $\text{Cs} \rightarrow \text{D}_2$ are measured. L. J. J.

Atomic-ray apparatus for luminous excitation of elements which are volatilised with difficulty. W. Paul (*Z. Physik*, 1941, 117, 774—788).—The inverse Stark effect in the Cr I resonance multiplet at 4254 Å. is measured at field strengths of 200—300 kv. per cm. by absorption measurements in a Cr at. beam. The red displacements at field strengths 206, 234, and 275 kv. per cm. are 1.6, 2.1, and $2.9 \times 10^{-3} \text{ \AA}$. The effect is in agreement with Lochte-Holtgreven's data. Measurements of the hyperfine structure of the Be II resonance line at 3130 Å., obtained in emission by excitation of a beam of at. Be by electron bombardment, give a val. between -0.4 and -0.8 for the g factor of the Be nucleus. (See also C., 1944, Part 2.) L. J. J.

Radiation fields of Pr^{++} and Nd^{++} ions in hexagonal salt crystals. K. H. Hellwege (*Z. Physik*, 1941, 117, 198—204).—Analysis of 34 lines in the spectra of cryst. $\text{Pr}_2\text{Zn}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ and $\text{Nd}_2\text{Zn}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, in which only electronic transitions are involved, shows that electrical dipole radiation is involved in every case. The results agree with Van Vleck's theory of forbidden transitions in crystals assuming a cubic crystal field. L. J. J.

Absorption spectra of the iron group. I. B. Borovski and E. E. Vainshtein (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 38, 130—132).—Special attention is called to the influence of symmetry of the wave function of the initial state of transition $\psi_i (KL_1 - 1s; 2s; L_{II, III} - 2p)$ on the intensity of distribution in the fundamental edge and at a distance of 50 e.v. from it. Thus for $W-L_1$ the edge has knicks on the long-wave regions without white lines on the short-wave side. For $W-L_{II}, W-L_{III}; \text{Cu}-L_{II}, \text{Cu}-L_{III}; \text{Ni}-L_{III}$ simple fundamental edges with bright white lines on the short-wave side exist, which are lacking in ^{50}Zn and ^{79}Au . A new method of analysis leads to an identification of the short-wave max. $(\nu/R)L_{II}L_{III}$ with the line $(\nu/R)L_1$ of the L_1 edges, and the inflexion lines are hence found to shift 6—8 e.v. For ionic compounds the max. of the absorption lines on the frequency scale is shifted only 1.5 to 1.2 e.v., but the shift of the (ν/R) term reaches 7 e.v. for ions of max. valency. J. O'M.-B.

Stark effect in the strontium I resonance line at 4607 Å. H. Koppermann and C. Otzen (*Z. Physik*, 1941, 117, 156—167).—The method described in the preceding abstract has been applied to the Stark effect in Sr I. The σ and π components are displaced, respectively, towards the violet and red. The displacement is $\propto X^2$ in the range 100—300 kv. per cm. The $5p^1P_1$ and $5s^1S_0$ terms are split to comparable extents. The displacements found are those predicted by theory, e.g., $\Delta\nu = 0.0104 \text{ cm}^{-1}$ for σ and 0.0320 cm^{-1} for π . L. J. J.

Theory of the continuous X-ray spectrum: short-wave limit. R. Weinstock (*Physical Rev.*, 1943, [iii], 64, 276—278).—Mathematical. By passing to the limit of zero velocity for the scattered 73 D (A., I.)

electron, an earlier result (cf. A., 1942, I, 310) for the intensity distribution of continuous X-radiation is reduced to apply at the short-wave limit. N. M. B.

Compton effect and the hole theory. J. Smorodinski (*J. Physics U.S.S.R.*, 1943, 7, 92).—The cross-section of the Compton effect calc. by Bhabha *et al.* (A., 1942, I, 384) on the basis of the hole theory is incorrect, and their conclusions concerning inconsistency in the Dirac theory are unfounded. A. J. M.

Measurements on selenium rectifiers and barrier-layer cells (an experimental contribution to Schottky's boundary-layer theory). (Frl.) A. Schmidt (*Z. Physik*, 1941, 117, 754—773).—Measurements of rectification characteristics as functions of applied potential, and temp.-dependence of barrier-layer resistance and capacity, show that Se rectifiers can be assumed to have a barrier layer in the "exhaustion region," the effect being modified by field emission effects at the metal-semiconductor boundary. The closest approach to theoretical behaviour is obtained when the covering metal has a small val. for the work of emission of defect-electrons, e.g., Bi and Au. The postulates of Schottky's boundary-layer theory are fulfilled by Se rectifiers, so that a "physical" barrier layer is produced by the electronic effect of the covering metal. L. J. J.

Quantum mechanics of secondary electron emission from transition metals. H. Schlechtweg (*Naturwiss.*, 1943, 31, 204—206).—The quantum-theoretical basis of the emission of secondary electrons is connected with the Coulomb interaction between the primary electrons and the metal electrons which are not in the states of the metallic lattice. Two cases are distinguished: (a) true metals with completed inner shells, and (b) transition metals, in which the s -band overlaps the d -band of the conductivity electron. The scattering of the primary electrons at the metal electrons is dealt with by the Born approximation. The unperturbed eigenfunction of a system consisting of an s -electron and a primary electron is obtained, and a similar expression holds for d -electrons. The probability of the occurrence of $s \rightarrow d$, $s \rightarrow s$, and $d \rightarrow d$ transitions is considered. A. J. M.

Theory of static fields. I. Phenomenological attempt to determine the proper field of an electron. G. Beck (*Physical Rev.*, 1943, [ii], 64, 366—375).—Mathematical. N. M. B.

Effect of space charge on electron beams. J. Aharoni (*Phil. Mag.*, 1944, [vii], 35, 36—50).—Mathematical. H. J. W.

Theory of electrical electron microscope for objects emitting electrons. A. Recknagel (*Z. Physik*, 1941, 117, 689—708).—A method of calculating the paths of electrons emitted from a surface is derived and used to form an image of the surface, without the assumption that the paths of the electrons are throughout nearly parallel with the optic axis. L. J. J.

New form of field electron emission at very low pressures from metallic surfaces dusted with insulating substances. H. Paetow (*Z. Physik*, 1941, 117, 399—408).—When a fine insulating powder, e.g., Al_2O_3 , MgO , S , or bakelite, is spread on the cathode of a discharge tube evacuated to 10^{-3} — 10^{-7} torr., and a discharge started at $\sim 1000 \text{ v.}$, the cathode becomes uniformly covered with a thin film of particles $< 1 \mu$. in diameter, and acquires a high electron emissivity at low potentials, e.g., $\sim 100 \text{ ma. per sq. cm. at } 200 \text{ v.}$ The emissivity persists over the pressure range 10^{-4} — 10 torr. L. J. J.

Micro-analysis by electrons. J. Hillier (*Physical Rev.*, 1943, [ii], 64, 318—319).—A special form of electron micro-analyser is described for investigating the velocity distribution of the electrons transmitted by thin collodion films. With 15—50-kv. electrons and irradiated masses of 10^{-14} — 10^{-16} g. , the velocity losses due to the excitation of the K -levels of C, N, and O were observed, and those of Be, Al, and Si were detected, the last two being weak. The K -level excitation of Fe could not be detected, but the L -level was sharp and strong. A line, presumably due to an M -level excitation of Fe, was observed. N. M. B.

Statistics of multiple collisions. F. Moglich and R. Rompe (*Z. Physik*, 1941, 117, 119—124).—The temp. coeff. in the expression for the frequency of multiple collisions between electrons and sound quanta in a solid is calc. on the basis of maintenance of thermodynamic equilibrium, in accordance with Planck's formula.

Velocity formula in electronic theory of metals. W. Glaser (*Z. Physik*, 1941, 117, 20—22).—An electronic velocity formula is derived directly from the quantum-mechanical definition of current.

L. J. J.

Electrical conduction in metals. I. Supek (*Z. Physik*, 1941, 117, 125—144).—Mean free paths of conduction electrons are calc. by a treatment analogous to the kinetic theory of gases. Expressions are derived for the sp. conductivity over the whole temp. range, agreeing with Bloch's expressions at high and low temp.

L. J. J.

Activation of nitrogen in the presence of mercury. S. S. Joshi and A. Purushotham (*Proc. Indian Acad. Sci.*, 1943, 18, A, 218—221).—N₂ at a pressure of a few cm. was passed through a discharge tube (D₁) with Al electrodes, then through a second tube (D₂) with one Hg electrode, and finally over a powdered I indicator. When D₁ was excited, but not D₂, an after-glow was observed in D₂ at ordinary temp. With D₂ at 140° the Hg luminescence increased to such an extent (owing to collisions of the second type) as to mask the N₂ after-glow, but the I indicator showed that the N₂ was still excited. When D₂ alone was excited at 30° the N₂ after-glow was observed, strongly enough to be identified spectroscopically, over a wide range of pressures. With D₂ at 160° there was an intense after-glow, due to collisions with metastable Hg atoms.

H. J. W.

Effect of metastable excited states on the normal current density and normal cathode potential fall in glow discharges in rare gases and rare-gas mixtures. J. Meissner (*Z. Physik*, 1941, 117, 325—343).—The effect of pressure on the cathode potential fall and c.d. is in accordance with similarity laws in pure rare gases, but in Ne-A mixtures both characteristics fall to low vals., and deviations from the similarity laws occur. Addition of 0.5% of A to Ne eliminates contraction in the discharge. The deviations are ascribed to a cathode surface effect. Large differences between cathode fall and min. p.d. for the initiation of the discharge in gases with metastable excited at. states are due to liberation of electrons from the cathode by metastable atoms.

L. J. J.

Relative abundance of the isotopes of potassium in Pacific kelps and in rocks of different geologic age. K. L. Cook (*Physical Rev.*, 1943, [ii], 64, 278—293).—In view of reported variations in the relative abundance of the stable isotopes of O, C, and K, investigations on the ³⁹K/⁴¹K ratio were made with a Dempster double-focussing mass spectrograph. To 1% accuracy, the ratio for kelps, Upper-Cambrian fossils, and rocks of early pre-Cambrian to Tertiary age shows no measurable variation. The average val. is 14.12 ± 0.28. Fluctuations are attributed to isotope effects of the hot-filament ion source.

N. M. B.

Isotope distribution in molybdenum and validity of the reciprocity law. H. Lichtblau and J. Mattauch (*Z. Physik*, 1941, 117, 502—509).—The reciprocity law is not valid for all types of plates used in mass-spectroscopy, but for the plates used by the authors the Schwarzschild exponential law holds. This only slightly reduces the discrepancy between their results and those of Hönigschmid and Wittmann (A., 1936, 1439).

L. J. J.

Molybdenum isotopes produced by the disintegration of uranium. O. Hahn and F. Strassmann (*Z. Physik*, 1941, 117, 789—800).—The products of artificial disintegration of U are: (i) a 12-min. Mo, giving a very short-lived isotope of Ma, and (ii) a 14-min. Mo, giving a 14-min. Ma isotope. The previously reported 18-min. Mo is a mixture of the above. The 67-hr. Mo previously described is verified.

L. J. J.

Exclusion rule for neutron and proton emission from nuclei with an odd charge. C. F. von Weizsäcker (*Naturwiss.*, 1943, 31, 207—208).—The ³¹P nucleus can break down into ³⁰Si with proton emission, or into ³⁰P with neutron emission. There are twice as many resonances in the case of neutron emission as in that of proton emission. The resonances in the case of neutrons can be regarded as two pairs of doublets, and the proton resonances have the same energy as one of the components of the doublet. A similar phenomenon is observed with ³¹Na. Both the ³¹P and the ³¹Na nuclei have, in addition to α -particles, 2 neutrons and 1 proton. The above facts can be explained on the assumption that the two states of the doublet differ only in the mutual spin orientation of these three "excess" particles, and that the remainder of the nucleus, after emission of the proton or neutron, remains in the ground state. There are three possible states, in which the spins of the three particles differ. The possible transitions are discussed, and exclusion rules are considered.

A. J. M.

Maximum energy of β -rays of some isotopes produced by fission of uranium. H. J. Born and W. Seelmann-Eggebert (*Naturwiss.*, 1943, 31, 201—202).—Approx. vals. for the max. energy of β -rays from 17 isotopes produced by fission of U have been obtained by consideration of absorption curves of rays of known energy (E), and two characteristic curves, one giving the connexion between max. range and E (used when the prep. was sufficiently active), the other giving the dependence of half-val. thickness (mass of Al per sq. cm. which reduces initial intensity to one half) on E .

A. J. M.

Energies of the γ -rays from ¹²⁷Sb, ¹¹⁵Cd, ¹⁹²Ir, ⁵⁴Mn, ⁶⁵Zn, and ⁶⁰Co. C. E. Mandeville and H. W. Fulbright (*Physical Rev.*, 1943, [ii], 64, 265—267).—The distributions in momentum of Compton recoils arising from γ -rays emitted in the disintegration of radio-elements were obtained by coincidence counting in a magnetic spectrograph. From the end-points of the distributions the calc. quantum energies in Me.v. are, respectively, 0.80, 0.65, 0.63, 0.86, 1.14, each ± 0.02, and 1.33 ± 0.03.

N. M. B.

Disintegration schemes of radioactive substances. V. ¹³⁰I. A. Roberts, L. G. Elliott, J. R. Downing, W. C. Peacock, and M. Deutsch (*Physical Rev.*, 1943, [ii], 64, 268—275; cf. Livingood, A., 1939, I, 54; Tape, A., 1940, I, 53).—The decay of ¹³⁰I, studied by spectrometer and coincidence methods, proceeds by two modes of negatron emission of max. β -ray energy 0.61 ± 0.02 and 1.03 ± 0.02 Me.v. The high-energy spectrum represents 60 ± 10% of the disintegrations and is accompanied by γ -rays of energies 0.537 ± 0.005, 0.667 ± 0.008, and 0.744 ± 0.010 Me.v. The low-energy spectrum is accompanied by the same three γ -rays and by a γ -ray of energy 0.417 ± 0.005 Me.v. The coeffs. of internal conversion in the K shell are 0.0031, 0.0038, 0.0069, and 0.012 (± 20%) in order of decreasing γ -ray energy. The conversion in the L shell is much smaller. The Fermi plot of the complex spectrum can be separated into straight lines which may be extrapolated to obtain the correct disintegration energies.

N. M. B.

Disintegration schemes of radioactive substances. VI. ⁵⁶Mn and ⁵⁶Co. L. G. Elliott and M. Deutsch (*Physical Rev.*, 1943, 64, [ii], 321—331).—Both nuclei decay to stable ⁵⁶Fe, which has excited states with excitation energies 0.845, 2.11, 2.66, and 2.98 Me.v. De-excitation of the three high-energy states always leads to the 0.845 level and thence to the ground state. The negatron spectrum of ⁵⁶Mn consists of groups with max. energies 2.86, 1.05, and 0.73 Me.v., and relative abundance 60 : 25 : 15, leading to the first, third, and fourth of the above excited states. The positron spectrum of ⁵⁶Co consists mainly of a single group of max. energy 1.50 Me.v. leaving the ⁵⁶Fe nucleus in the 2.11-Me.v. state. Orbital electron capture also takes place involving several other excited states. Energies of 8 γ -rays emitted by ⁵⁶Fe are 0.845, 1.26, 1.74, 1.81, 2.01, 2.13, 2.55, and 3.25 Me.v., apparently multiples 2, 3, 4, 5, and 6 of 0.425 Me.v. The β -ray spectra have "allowed" Fermi-theory shape, and this and probability of orbital electron capture are discussed in terms of tensor interaction. Mass differences between neutral atoms, obtained from disintegration schemes, are ⁵⁶Mn — ⁵⁶Fe = 3.98, and ⁵⁶Co — ⁵⁶Fe = 4.96, and the threshold for the reaction ⁵⁶Fe(p, n)⁵⁶Co 5.47 Me.v.

N. M. B.

Occurrence of isomeric atomic nuclei. (A) J. Mattauch. (B) S. Flüge (*Z. Physik*, 1941, 117, 246—255, 255—256).—(A) It is concluded empirically that the energetically favoured g - g nuclei possess no isomerides. Isomerides exist in the case of nuclei with spin $> 9/2 \cdot h/2\pi$ in the ground state; this should hold for the stable ²⁰⁹Bi isotope.

(B) The significance of the above conclusions is discussed.

L. J. J.

Theory of nuclear isomerism. N. Koyenuma (*Z. Physik*, 1941, 117, 358—374).—Integrations over the spherical functions corresponding to individual rotational impulses, necessary for the calculation of matrix elements for γ -transition probabilities, are given for $l = 0$ to $l = 6$.

L. J. J.

Distribution and dissipation curves for ultra-radiation impact transmitted from air to lead, iron, and aluminium. H. Schmid (*Z. Physik*, 1941, 117, 452—481).—Distribution and dissipation curves for impacts generating > 136,000 ion-pairs (> 10 corpuscles) in Pb, Fe, and Al targets have been determined with a thin-walled pressure ionisation chamber and a tube-electrometer. Dissipation curves for Fe and Al can show two max., whereas those for Pb show one max. only except at the highest energies. Max. are at 2.25 cm. for Pb, 4.5 and ~10 cm. for Fe, and ~6.5 and ~35 cm. for Al. The effect is ascribed to the superposition of two processes, the first involving a multiplication of the shower, the second caused by mesotrons.

L. J. J.

II.—MOLECULAR STRUCTURE.

Band spectrum of carbon deuteride. L. Gero (*Z. Physik*, 1941, 117, 709—721).—Rotational analyses are made of the (0, 0) and (1, 1) bands of the A² $\Delta \rightarrow$ X² Π system of CD, the (0, 0), (1, 1), and (2, 2) bands of the C² $\Sigma \rightarrow$ X² Π system, and the (0, 0), (1, 0), and (1, 1) bands of the B² $\Sigma^+ \rightarrow$ X² Π system. Predissociation is indicated in the upper states of each band system. Band-origins, rotational consts., and spin- and A-splitting are calc.

L. J. J.

Rotational analysis of the emission spectrum of CuF. L. H. Woods (*Physical Rev.*, 1943, [ii], 64, 259—264).—The emission spectrum of gaseous HF at ~0.1 mm. pressure in a hollow Cu cathode was examined at 7000—2000 Å. and showed an unknown band of widely spaced lines at 2450—2600 Å., thought to be the ² $\Sigma \rightarrow$ ² Π transition of HF⁺. From the same source the emission spectrum of CuF, obtained and photographed, showed band systems at 5700, 5060,

and 4920 Å. A rotational analysis shows that the three systems have the same lower state and are of the types ${}^1\Pi \rightarrow {}^1\Sigma$, ${}^1\Sigma \rightarrow {}^1\Sigma$, and ${}^1\Pi \rightarrow {}^1\Sigma$. Consts. for the states are reported. The calc. rotational isotope effect accords with the experimental val. N. M. B.

ε band-system of the NO molecule. L. Gero, R. Schmid, and K. F. von Szily (*Naturwiss.*, 1943, 31, 203).—Emission photographs with NO, using a 21-ft. grating, give the ε-absorption bands with considerably greater intensity than the γ bands. Rotation analysis of the bands at 2021 and 2091 Å. shows that their lower states are the $v'' = 2$ and $v'' = 3$ levels of the NO ${}^2\Pi$ ground state. The two bands have a common upper state, the rotation const. B being 1.99 cm.⁻¹. This is somewhat > the B'_0 val. of the γ bands. The bands which are given in Guillery's term scheme (A., 1927, 496) as $v' > 3$ therefore belong to a separate ε band system. A. J. M.

Intensity distribution in quartet-doublet bands. II. I. Kovács and A. Budó (*Z. Physik*, 1941, 117, 612–620).—Intensity distribution in the branches of quartet-doublet bands ${}^4\Pi(a) \rightarrow {}^2\Sigma$, ${}^4\Pi(b) \rightarrow {}^2\Sigma$, ${}^4\Pi(a) \rightarrow {}^2\Pi(a)$, ${}^4\Pi(a) \rightarrow {}^2\Pi(b)$, ${}^4\Pi(b) \rightarrow {}^2\Pi(a)$, and ${}^4\Pi(b) \rightarrow {}^2\Pi(b)$ is calc. L. J. J.

Infra-red absorption spectrum of methylene bromide vapour. D. Barca-Gălatcanu (*Z. Physik*, 1941, 117, 589–595).—The absorption spectrum of CH₂Br₂ in the region 1.5–15 μ. has been measured. The bands at $\nu\nu$ 3001, 3070, and 1361 cm.⁻¹ are regarded as CH₂ fundamentals corresponding to the Raman bands 2986, 3050, and 1390 cm.⁻¹. Bands at $\nu\nu$ 813, 1144, and 1232 cm.⁻¹ are ascribed to the mutual fundamental vibrations of the CH₂ and CBr₂ groups. L. J. J.

Absorption spectrum of chromyl fluoride vapour. K. H. Hellwege (*Z. Physik*, 1941, 117, 596–601).—The absorption spectrum of CrO₂F₂ is qualitatively very similar to that of CrO₂Cl₂, with at least five diffuse bands repeated ~20 times in the region 17,500–21,500 cm.⁻¹, with a period of 200 cm.⁻¹, compared with 136 cm.⁻¹ for the chloride. The period is identified with a vibration frequency. L. J. J.

Absorption spectra of some organic solutions in the vacuum ultra-violet. J. R. Platt, I. Rusoff, and H. B. Kleven (J. Chem. Physics, 1943, 11, 535–544).—By the use of *n*-C₆H₁₄ and *n*-C₈H₁₈ as solvents, it is possible to investigate the ultra-violet absorption of org. compounds down to 1700 Å. in 0.3-mm. cells, with a fluorite spectrograph. The transmission limits in such cells have been determined for a no. of solvents, including H₂O, EtOH, MeOH, *n*-C₆H₁₄, *n*-C₈H₁₈, Et₂O, COMe₂, and *iso*-C₈H₁₈. Absorption curves of some alcohols, ethers, ketones, acids, BuⁿCHO, and Δ⁷-octene (I) are given. The double-bond peak at 1840 Å. for (I) is clearly obtained. A. J. M.

Glass structure according to infra-red absorption spectra. J. I. Gerlovin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 126–127).—Glass films of thickness ~10 μ. show a strong absorption max. at 9–10 μ., and fused quartz at 9 μ. This supports the assumption that silicate glasses consist of SiO₄ tetrahedra. A band at 12–13 μ. indicates a ring structure of the tetrahedra. Addition of metal oxides causes the max. of the bands to become more diffuse and to shift to longer λ. Results indicate that glass has cryst. properties which diminish as the composition becomes more complex. N. M. B.

Relation between chemical composition and glass transmission in the infra-red. J. I. Gerlovin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 170–172).—30 borate, 20 silicate, and 4 phosphate glasses, and vitreous SiO₂ and B₂O₃ (with 0.5% PbO to prevent decomp. turbidity), were investigated. Silicate systems show the greatest transmission, with a broad feeble transmission band for Pb silicate glasses at 2.8–3.8 μ. Borate glasses show absorption bands at 2.85 and 3.7 μ. and, for lighter glasses, at 2.2 and 2.4 μ.; B₂O₃ has the least transmission. Phosphate glasses show absorption at 2.2 to a max. at 3.5 μ. Fused quartz has a sharp absorption max. at 2.7 and a feeble max. at 3.7 μ. In all cases, addition of metal oxides to the glasses increases the transmission, the increase being more marked in passing from light- to heavy-metal oxides. N. M. B.

Polarisation of fluorescence and anisotropy of molecules of organic dyes. P. P. Feofilov (*J. Physics U.S.S.R.*, 1943, 7, 68–79).—Curves showing the dependence of polarisation of fluorescent light on the λ of the exciting light (polarisation spectra) are obtained for rhodamine-B, Na fluorescein, Na eosin (I), trypanflavine (II), acridine-orange (III), benzoflavin (IV), Na perylenetetracarboxylate, aesculin, and pinakryptol-yellow. These polarisation spectra are sp. for each dye. For (I)–(IV) the variation of dichroism of oriented mols. with λ is investigated, and there is a correspondence between this and the polarisation spectrum. This indicates that the angles between emitting and absorbing oscillators are not produced during the excitation, but are inherent in the mol. The anisotropy of the mols. can be interpreted by means of an oscillator model in which the fluorescing mol. is regarded as an emitting oscillator with a no. of absorbing oscillators rigidly coupled to it. A. J. M.

Fluorescence of chlorophyll. Effects of concentration, temperature, and solvent. F. P. Zscheile and D. G. Harris (*J. Physical Chem.*, 1943, 47, 623–637).—Fluorescence spectra of chlorophyll-*a* (I) in 13 solvents and of chlorophyll-*b* in Et₂O were investigated. With

increase in concn. max. absorption shifts towards the red as a result of reabsorption of fluorescence. Fluorescence intensity decreases with time of exposure to the source of excitation, the intensity recovering after a period of darkness in the case of some solutions, e.g. in C₆H₆. With decrease in temp. the fluorescence max. of Et₂O solutions of (I) shifts towards the red and the fluorescence intensity increases. C. R. H.

Decay of phosphorescence of crystalline phosphors. M. Schön (*Naturwiss.*, 1943, 31, 203–204).—The decay curves for phosphorescence of two cryst. ZnS phosphors with the same activator eventually become exponential. This can be explained on the theory of radiationless reversibility of electrons in the excited activator. Since the radiationless transitions are α the concn. (*n*) of electrons, and the transition giving rise to the glow is α *n*², a point must be reached in the course of the decay when the recombination of electrons with the excited activator must be decided by the *n* term. The reaction mechanism is then almost exclusively unimol., and the decay curve becomes exponential. The fact that only two of the phosphors give this exponential curve agrees with the fact that radiationless transitions depend greatly on structure. The onset of the exponential decay takes place earlier at higher temp. A. J. M.

Luminescence of phosphors at the moment of excitation. V. V. Antonov-Romanovski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 125–129).—On the cessation of excitation the intensity of luminescence of CdSiO₃ and CdB₂O₅ powders activated by Mn falls at once to ~0. The luminescence increases quite smoothly from 0, so that the fall is not explicable by the presence of fluorescence. The kinetics of phosphorescence are examined; the simple bimol. theory can account for these results. A limited general comparison with experimental data is given, but this is hindered by experimental difficulties such as the (unknown) quenching properties of the exciting light. J. O'M.-B.

Phosphorescence and scintillation spectra. W. Kutzner (*Z. Physik*, 1941, 117, 575–588).—Comparison of phosphorescence spectra of ZnS phosphors produced by ultra-violet irradiation (<3700 Å.) with spectra of scintillations produced by impact of α-particles shows that both spectra are compounded of the same six bands, with max. intensities at 4650, 4800, 5200, 5560, 5930, and 6450 Å. Spectra obtained with phosphors containing different activators, or with different methods of excitation, show different relative intensities in the six bands. The shorter-λ bands are more prominent with α-ray excitation. These effects indicate that both spectra originate in the same source, i.e., Zn or S atoms. L. J. J.

Structure of halide phosphors containing tin. M. Hüniger and J. Rudolph (*Z. Physik*, 1941, 117, 81–99).—Luminescence in alkali, alkaline-earth, and NH₄ halides containing small amounts of Sn^{IV} halides is excited by the same λλ as are absorbed by single crystals of the phosphors and by conc. aq. solutions containing the halides with additions of Sn as completely co-ordinated complex salts. The no. of luminescence centres, determined from absorption measurements, is ~10⁻⁴–10⁻⁵ per halide mol. The emission spectra resemble those produced in reduction of Sn^{IV} halides by alkali-metal vapours. A. J. M.

Raman spectrum of glycine, its dependence on pH, and the possibility of its analytical use. J. Goubeau and A. Lünig (*Ber.*, 1940, 73, [B], 1053–1058).—The Raman spectrum of glycine (I) is recorded from pH 13 to pH 0. (I) exists as NH₂·CH₂·CO₂⁻ at pH <11.5, as ⁺NH₃·CH₂·CO₂⁻ at pH 9.4, and as ⁺NH₃·CH₂·CO₂·H at pH <1. Spectra of hydrolysates from gelatin and peptone indicate presence of (I), but other lines are also present. Raman spectra can probably be used generally to detect (I) (cf. C., 1944, Part 2; also Wright *et al.*, A., 1937, I, 282). R. S. C.

New experimental data on the structure of the Rayleigh line in benzene. M. F. Vuks (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 120–125).—Data obtained by a new method of investigating the distribution of intensity within the Rayleigh line, based on measuring the absorption of light passing through a resonance filter, are reported for C₆H₆. The calculation of the shape of the line from these data is given. N. M. B.

Electrostatic contribution to hindered rotation in certain ions and dipolar ions in solution. I, II. T. L. Hill (*J. Chem. Physics*, 1943, 11, 546–551, 552–557).—I. Effective dielectric const. (ε_g) are calc. for H₂C₂O₄, (CH₂·NH₂)₂, glycine, α-alanine, leucine, and NH₂·CHEt·CO₂·H from the experimental dissociation const. and structural parameters. The electrostatic contribution to hindered rotation can be calc. from the ε_g. In the case of H₂S₂O₆, for which the dissociation const. are unknown, an approx. val. of ε_g (30) and sp. locations of point charges in the mol. are assumed. The electrostatic potential barriers are considered, and the ionic equilibria in H₂S₂O₆ are discussed.

II. The method used for the above work is extended to mols. with an additional angle of rotation {NH₂·[CH₂]₃·NH₂, CH₂(CO₂H)₂, β-alanine, and H₄P₂O₇}. The electrostatic contribution is considerably less important than other factors, and may be negligible in some cases. It is probable that in the cases of H₄P₂O₇ and

$\text{H}_2\text{S}_2\text{O}_8$, the treatment is over-simplified and that one ϵ_{B} is insufficient for a complete solution of the problem.

A. J. M.

Polymorphism and dielectric constant. S. D. Gokhale, N. L. Phalnikar, and S. D. Bhawe (*J. Univ. Bombay*, 1943, 12, A, Part 3, 75—80).—The dielectric const. (ϵ) of solid, fused, and supercooled liquid resorcinol, *o*- and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, and *o*- and *p*- $\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{OH}$ was measured at λ 520 and 90 m. and at various temp., and from the inflexions in the ϵ - T curves the transition temp. between the unstable β - and stable α -forms are deduced. With *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ the transition point is 35°. With *p*- $\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{OH}$ there are two forms, of m.p. 41° and 33°, respectively, but no definite transition point is detected. In other cases the results are in accord with previous observations.

J. W. S.

Behaviour of solids in high-frequency electric rotating fields. H. Hartmann and W. Stürmer (*Naturwiss.*, 1943, 31, 206).—According to Debye, a body suspended in a rotating electric field should experience a turning moment if the frequency of the field is of the order of a dispersion frequency of the body. The effect of rotating fields of λ 1.2—5 m. on vinidur, calcite, paraffin, alberite, COPH_2 , *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, and *p*- $\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{NO}_2$ has been investigated, and the variation of turning moment with frequency has been determined.

A. J. M.

Nature of the chemical bond in some inorganic compounds. G. B. Boki and E. E. Vainshtein (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 307—309).—The very short Al—Al and Pt—Pt distances 0.64 Å. and 1.4 Å., respectively, in $(\text{AlCl}_3)_2$ and $\text{cis}[\text{Pt}(\text{NH}_3)(\text{C}_2\text{H}_4)\text{Cl}]_2$ can be explained by a new type of intermetallic linking involving 2*p* and 5*d* electrons, respectively, corresponding with calc. vals. 0.35 and 0.71 Å. for the at. radii. A similar linking is predicted for B.

L. J. J.

General theory of fluctuations. H. Scheffers (*Z. Physik*, 1941, 117, 444—451).—A general parameter of state is included in a statistical treatment of generalised thermodynamic theory.

L. J. J.

Derivation of Trouton's rule. M. S. Telang (*J. Indian Chem. Soc.*, 1943, 20, 271—276).—Methods of deriving Trouton's rule are reviewed, and a new derivation, based on empirical rules of Guldberg ($T_{\text{B}} = \sim 0.66T_{\text{e}}$) and Sugden ($V_0 = 0.27V_{\text{e}}$) and Sugden's density-temp. relation, is given.

F. J. G.

III.—CRYSTAL STRUCTURE.

Rules for the conventional orientation of crystals; a correction. J. D. H. Donnay (*Amer. Min.*, 1943, 28, 470; cf. A., 1943, I, 272).

L. S. T.

Vitreous state. M. L. Huggins, K. H. Sun, and A. Silverman (*J. Amer. Ceram. Soc.*, 1943, 26, 393—398).—The difficulty of strictly defining the vitreous state and certain border-line cases is briefly discussed. The vitreous states of SiO_2 , SiO_2 glasses, S, Se, B_2O_3 , P_2O_5 , etc., glucose, and polyvinyl alcohol (H-bridges), and the org. polymers, are described in some detail.

J. A. S.

Structure of vitreous substances. E. A. Porai-Koschitz (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 267—269).—X-Ray observations indicate the presence of individual crystallites of $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$ and of quartz in an $\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3\cdot\text{SiO}_2$ glass.

F. J. G.

Linkages in metallic calcium. P. Gombás (*Z. Physik*, 1941, 117, 322—324).—The author's theory of metallic lattices is employed for the determination of the chief lattice characteristics of Ca. Theoretical and experimental vals. for the radius of the elementary sphere in the equilibrium position of the atom, for the sum of the first and second ionisation energies of Ca, and for the sublimation energy of metallic Ca, respectively, are: 2.19, 2.17 Å.; 456.2, 452.4 kg.-cal. per g.-mol.; 43.0, 39.2 kg.-cal. per g.-mol.

L. J. J.

Chemistry of oriented growth of crystals of organic compounds. I. Oriented growth of anthraquinone on antimony. J. Willems (*Naturwiss.*, 1943, 31, 208—209).—It is possible to grow anthraquinone (I) crystals from C_6H_6 solution on a (0001) face of Sb in three positions. (I) separates in needle-shaped crystals with the long axis parallel to the (0221) or (0112) axes of the Sb.

A. J. M.

Isomorphism of organic compounds.—See A., 1944, II, 100.

Model substance for silicates. H. O'Daniel and L. Tscheischwill (*Naturwiss.*, 1943, 31, 209—210).— β -Wollastonite (CaSiO_3) resembles NaBeF_3 in structure. Unit cell dimensions are given for both compounds; both have 12 mols. per unit cell and space-group C_{2h} . Be_2F_3 is a possible structural element in some beryllifluorides. The compound $\text{Na}_2[\text{LiBe}_2\text{F}_7]$ (I) can be obtained from the ternary system $\text{LiF}\text{--}\text{NaF}\text{--}\text{BeF}_2$. Its powder diagram resembles that of gehlenite, $\text{Ca}_2[\text{AlSiAlO}_7]$. Be_2F_3 double tetrahedra are present as structural elements in (I).

A. J.

Structural type of perovskite (CaTiO_3). S. von Náyay-Szabó (*Naturwiss.*, 1943, 31, 202—203).—Oscillation photographs with Cu K α radiation (and some with Mo K α radiation) have been obtained and agree with a pseudo-cubic unit cell, a 7.60 Å. Perovskite was formerly supposed to belong to the G5 type, but calculation based

on Goldschmidt's ionic radii shows that the lattice is monoclinic; space-group $\text{C}_{2h}^2\text{--}P_{21/m}$. Other substances of the perovskite type (ABO_3) have also been investigated. For many the type is G5 (e.g., BaTiO_3 , a 3.98 Ti—O 1.99 Å.; BaSnO_3 , a 4.10, Sn—O 2.05 Å.; BaZrO_3 , a 4.19, Zr—O 2.09 Å.). The Goldschmidt radius for Zr^{4+} (0.87 Å.) is corr. to 0.77 Å. PbZrO_3 (a 9.28 Å.) and CdSnO_3 (a 7.80 Å.) belong to the new perovskite type. The existence of the two types is due to the fact that the ions are arranged in the closest packing.

A. J. M.

Crystal structure of braunite, $3\text{Mn}_2\text{O}_3\cdot\text{MnSiO}_3$.—See A., 1944, I, 72.

Interpretation of the crystal structure of cementite. N. J. Petch (*J. Iron and Steel Inst.*, Feb., 1944, *Advance copy*, 8 pp.).—From X-ray examination of cementite (I), extracted from quenched steel (C 1.8%), it is suggested that (I) is essentially a framework of close-packed Fe atoms held together by metallic bonding, with the small C atoms in the largest interstices, these atoms also being held in position by bonding which has a certain degree of metallic nature. Graphitisation of (I) is discussed.

T. D. F.

X-Ray analysis of a new type of complex compound of quadrivalent platinum. A. M. Rubinshtein and V. G. Kuznetsov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 85—92).—The double salt $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]\text{Cl}_2\cdot[\text{Pt}(\text{NH}_3)_4\text{NH}_2\text{Cl}]\text{Cl}_2$ (cf. A., 1941, I, 278) gives a powder X-ray diagram differing from those of its components and their mechanical mixture.

F. R. G.

X-Ray studies of supercooled ethyl alcohol. A. Prietzsch (*Z. Physik*, 1941, 117, 482—501).—X-Ray diffraction curves of EtOH at -150° show well-defined max. at $\sin \theta/\lambda$ 0.14, 0.22, and 0.4 and inflexions at ~ 0.3 and ~ 0.5 . Apparent radial density distribution curves show max. at 0.5, 1.4, 2.3, 2.7, 4.1, and 5.6 Å. In comparison with Harvey's results (A., 1940, I, 13) at 75° , the intramol. max. are very similar, whilst the intermol. max. are better defined. The no. of H linkings between O atoms is increased from 1.2 to 2 per mol., indicating formation of chains.

L. J. J.

Change of colour and optical properties of beryls on heating.—See A., 1944, I, 71.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Magnetic spectrum in infra-low frequency. S. S. Lavrentiev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 233—236).—The induction in a soft Fe wire in a sinusoidal magnetising field consists of a part in phase with the field and a part with a phase lag of 90° . Measurements of the corresponding permeabilities as functions of the period show that the in-phase permeability increases in the range of periods near 1 min., whilst the out-of-phase component exhibits a max. This behaviour is in agreement with Arkadiev's theory of magnetic viscosity.

H. J. W.

Preparation and properties of some compounds in the system $\text{H}_2\text{O}\text{--}\text{Na}_2\text{O}\text{--}\text{P}_2\text{O}_5$. E. Ingerson and G. W. Morey (*Amer. Min.*, 1943, 28, 448—455).—Optical properties of all known compounds of Na_2O and P_2O_5 are given. Some of the data are new. Crystallographic and ρ data and methods of prep. are also given for some of the compounds. Nomenclature is discussed. Vals. of n for 11 glasses in the system $\text{NaPO}_3\text{--}\text{Na}_4\text{P}_2\text{O}_7$ are recorded.

L. S. T.

Refractive index nomograph for liquid fatty acids. D. S. Davis (*Ind. Eng. Chem.*, 1943, 35, 1302).—From the data of Dorinson et al. (A., 1943, I, 119) a nomograph is constructed for determining the n of n -fatty acids from $\text{C}_8\text{H}_{17}\cdot\text{CO}_2\text{H}$ to $\text{C}_{17}\text{H}_{33}\cdot\text{CO}_2\text{H}$ at $\geq 80^\circ$.

J. W. S.

Melting time of safety fuses. III. J. A. M. von Liempt and J. A. de Vriend (*Z. Physik*, 1941, 117, 18—19).—"Inertia consts." are determined for a no. of metals and alloys. No difference is found between vals. for wires of circular and rectangular cross-section.

L. J. J.

Polymorphism of trilaurin. G. B. Ravitsch and G. G. Tzurinov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 314—316).—The smooth cooling curve of melted trilaurin shows an arrest at 35.5° , the m.p. of the α phase. The heating curve, after chilling to 26° , shows an arrest at 46.6° , the m.p. of the β phase, and after rapid chilling to 20° , an exothermal effect at 34.6° , ascribed to a transition of the α phase. Very rapid chilling to -15° showed an arrest at 20° and an exothermal effect at 15° . A liquid-cryst., γ , form is assumed, with m.p. $15\text{--}20^\circ$.

L. J. J.

Joule effects in air. H. D. Baker (*Physical Rev.*, 1943, [ii], 64, 302—311).—Joule effect determination methods are reviewed historically, and features of apparatus and technique necessary for precision measurements are analysed. Construction and operation of apparatus built to these requirements are described, and sample data for air are given and compared with available vals. It is concluded that with detail improvements the method developed will reach 0.1% accuracy.

N. M. B.

Viscosity of n -pentane. R. M. Hubbard and G. G. Brown (*Ind. Eng. Chem.*, 1943, 35, 1276—1280).—The viscosity (η) of liquid $n\text{-C}_5\text{H}_{12}$ is measured with a rolling-ball viscometer at $25\text{--}250^\circ$ and

15—1000 lb. per sq. in. pressure. The results are compared with previous data. The η of n -C₅H₁₂, determined at 26° with a Bingham capillary-tube viscometer, is 0.002296 ± 0.000005 poise.

J. W. S.

Viscosities at the b.p. of some primary amines, cyclohexane, and some of its derivatives. J. N. Friend and W. D. Hargreaves (*Phil. Mag.*, 1944, [vii], 35, 57—64).—Continuing previously reported work on the rheochor (R) (cf. A., 1943, I, 301), measurements of η for a series of primary amines give a mean $R = 20.6$ for NH₃. From cyclohexane and its derivatives it is concluded that ring formation is accompanied by a loss of from 4.4 to 6 units in R .

H. J. W.

Rigidity modulus of liquids and its dependence on temperature. M. Kornfeld (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 298—300).—Measurements of effective modulus of rigidity and angle of phase displacement between deformation and stress for rosin at -5° to 70° and frequencies 2.8×10^3 , 1.3×10^5 , and 2.9×10^6 Hertz show agreement with Maxwell's representation of shear as the sum of viscous and elastic components. The rigidity modulus decreases with increasing temp., and is $\leq 10^{10}$ dynes per sq. cm. L. J. J.

Critical shear stress [exerted on a sediment by a flowing fluid]. M. S. Quraishy (*J. Univ. Bombay*, 1943, 12, A, Part 3, 37—46).—Assuming that the force impressed on a layer of sand by a moving fluid \propto the gravitational force on the particles when falling freely in a stationary column of the fluid, a theory of the transport of sediment by fluid currents is derived. It leads to results in accord with observation.

J. W. S.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Thermal diffusion in mixtures of molecules of small mass difference. K. E. Grew (*Phil. Mag.*, 1944, [vii], 35, 30—36).—Three gaseous mixtures were examined in a Clusius-Dickel column. In Ne-NH₃, the Ne, if present in concns. $> 75\%$, diffuses down the temp. gradient, but this behaviour is reversed at lower concns. In A-HCl the heavier mol. always diffuses down the gradient, and in N₂O-CO₂ the N₂O does so. These results are discussed in terms of Chapman's theory (A., 1941, I, 201), and it is concluded that the mol. repulsions are not adequately represented by an inverse power law.

H. J. W.

Diffusion of hydrogen through iron in relation to the nature of the surface, and its connexion with catalysis. H. Betz (*Z. Physik*, 1941, 117, 100—118).—The diffusion of H₂ through an Fe cathode bombarded with H ions in a glow discharge is almost completely inhibited when the entry side of the Fe is abraded with emery, but is increased 2.4 fold when the exit side is so treated. The corresponding effects when the surface is ruled with parallel scratches, as a function of their distance apart, has been examined. The effect is attributed to return of the H into the discharge space from active centres on the sharp edges, where the recombination of H atoms is catalysed.

L. J. J.

Penetration of rare gases into metals. W. Bartholomeyczzyk, W. Funk, and R. Seeliger (*Z. Physik*, 1941, 117, 651—656).—Preliminary investigation of the removal of rare gases in discharge tubes at low pressures indicates that the gas penetrates into the cathode as ions, while the cathode metal is disintegrated and re-deposited by diffusion.

L. J. J.

Adiabatic compressibilities of some aqueous ionic solutions and their variation with indicated liquid structure of the water. V. B. Corey (*Physical Rev.*, 1943, [ii], 64, 350—357).—Vals. are reported for single concns. of aq. solutions of 27 strong electrolytes determined at 25° from sound velocity measurements at a supersonic frequency (1015.24 kc. per sec.), and show a marked correlation with corresponding vals. of the partial molal vol. of the solvent H₂O. The change in compressibility per mol. fraction of solute accords with X-ray and other indications of H₂O-structure change. There is strong evidence that H₂O has a liquid structure which becomes more highly co-ordinated and compact with the introduction of ions.

N. M. B.

Cyanamide as a solvent and reaction medium. E. C. Buckner (*Iowa State Coll. J. Sci.*, 1943, 18, 19—21).—Solvent properties of liquid CN-NH₂ are similar to those of H₂O. Anomalous results in conductivity measurements and compound formation are attributed to polymerisation of the solvent.

F. R. G.

X-Ray study of dissociation of an iron-copper-nickel alloy.—See A., 1944, I, 54.

Solubility of hydrogen in palladium. E. A. Owen (*Phil. Mag.*, 1944, [vii], 35, 50—57).—X-Ray investigations of the lattice changes when H is occluded by Pd at low pressures at 60—130° confirm the existence of a hysteresis effect. The X-ray reflexions from the β phase (rich in H) are always diffuse, even after annealing; this phase is thus finely divided. The α phase (Pd-rich) gives sharp reflexions which decrease in intensity as the H₂ pressure increases, but it is regenerated from the β phase during desorption in small aggregates giving diffuse lines. The results suggest a system not in thermal equilibrium. No evidence was found for the occurrence of metallic hydrides (cf. Lacher, A., 1937, I, 560).

H. J. W.

Solubility of water in liquid carbon dioxide. H. W. Stone (*Ind. Eng. Chem.*, 1943, 35, 1284—1286).—The solubility of H₂O in liquid CO₂ increases fairly regularly from 0.02% at -29° to 0.10% at 22.6° .

Solubility of lithium bromate and its hydrates. II. I. N. Averko-Antonovitch (*J. Gen. Chem. Russ.*, 1943, 13, 272—277).—Solubility data for LiBrO₃ (I) in the range -45° to the b.p. of the saturated solution (143°) are given. Above 52° (I) crystallises out and below 52° LiBrO₃.H₂O (II) is the stable solid phase, but supercooled solutions form very readily and exist as viscous syrups even at -70° . The conversion of (I) into (II) below 52° is slow and determination of the solubility of (I) in the metastable region as far as 4° was possible; solutions in contact with (I) could be kept for several days at -6° to -7° . Extrapolation below -45° on the ice-(II) f.p. diagram gave the eutectic point -47° at 54.5% of (I).

R. C. P.

Isolation of pure potassium nitrite from the commercial substance. T. M. Oza and B. R. Walavalkar (*J. Indian Chem. Soc.*, 1943, 20, 315—317).—Pure KNO₂ can be obtained by cooling (ice + NH₄Cl) with const. stirring a conc. solution of commercial KNO₃. After removal of mother-liquor from the crystals the operation is repeated with the liquor. The m.p. of pure KNO₂ is $407-408^\circ$. The solubilities at 0° and at the cryohydric point of ice and NH₄Cl are 34.3—34.5 and 31.5—31.8 g.-mol. per l. respectively, these vals. being $>$ those hitherto accepted.

C. R. H.

Solubility of ammonium persulphate in water and in solutions of sulphuric acid and ammonium sulphate. J. F. Gall, G. L. Church, and R. L. Brown (*J. Physical Chem.*, 1943, 47, 645—649).—Solubility (s) data at 15° and 20° for (NH₄)₂S₂O₈ in H₂O and in solutions of H₂SO₄ and (NH₄)₂SO₄ and mixtures thereof are recorded. [H₂SO₄] range from 0 to 400 and [(NH₄)₂SO₄] from 0 to 100 g. per l. s decreases with increase in [H₂SO₄] and [(NH₄)₂SO₄]. s in H₂O is 520 g. per l. at 15° and 542 g. per l. at 20°.

C. R. H.

Solubility of naphthalene in aqueous solutions of methyl, ethyl, *n*-propyl, and *n*-butyl alcohol at several temperatures. O. W. Mannhardt, R. E. De Right, W. H. Martin, C. F. Burmaster, and W. F. Wadt (*J. Physical Chem.*, 1943, 47, 685—702).—C₁₀H₈ solubility data at various temp. have been obtained for alcohol-rich aq. solutions of MeOH, EtOH, PrOH, and BuOH and used for the determination of the upper or, within the solubility gap, the upper two transformation temp. When considered in relation to published data they give a fairly good idea of the nature of the ternary ditectic surface, the line of three-phase monotectic equilibrium, and the ternary dichortic surface.

C. R. H.

Anthracene derivatives. V. Solubility of some salts of anthracene-mono- and -di-sulphonic acids. B. P. Fedorov and N. A. Lodigin (*J. Appl. Chem. Russ.*, 1942, 15, 164—172).—100 g. of saturated aq. solution contain at 20° the following amounts of the salts without hydrate H₂O: anthracene-1-sulphonic acid, K 0.41, Na 0.041, Ba (+3H₂O) 0.071, Ca (+3H₂O) 0.019, Mg (+4H₂O) 0.078, Pb (+2H₂O) 0.060, Zn (+6H₂O) 0.048; anthracene-2-sulphonic acid, K (+2H₂O) 0.16, Na 0.009, Ba 0.020, Ca (+H₂O) 0.016, Pb (+2H₂O) 0.007; anthracene-1:5-disulphonic acid, K (+2H₂O) 4.60, Na (+2H₂O) 2.51, Ba (+4H₂O) 0.37, Ca (+3H₂O) 0.27, Mg (+3H₂O) 0.15, Pb (+2H₂O) 0.22, Zn (+4H₂O) 0.15; anthracene-1:8-disulphonic acid, K (+H₂O) 2.32, Na (+3H₂O) 2.26, Ba (+4H₂O) 0.060, Ca (+5H₂O) 0.18, Mg (+3H₂O) 2.04, Pb (+2H₂O) 0.019, Zn (+3H₂O) 2.39; anthracene-2:6-disulphonic acid, K 1.64, Na (+H₂O) 1.21, Ba (+5H₂O) 0.046, Ca (+5H₂O) 0.24, Mg (+4H₂O) 0.12, Pb (+4H₂O) 0.048, Zn (+6H₂O) 0.054; anthracene-2:7-disulphonic acid, K 1.00, Na (+2H₂O) 1.09, Ba (+6H₂O) 0.90, Ca (+3H₂O) 0.11, Mg (+2H₂O) 0.067, Pb (+3H₂O) 0.80, Zn (+4H₂O) 0.57 g. Vals. for 100° are given also.

J. J. B.

Permutoids. H. Kautsky (*Kolloid-Z.*, 1943, 102, 1—14).—Permutoids, which are materials of such open lattice structure that gases and liquids can penetrate them and interact with their structural units, are discussed with particular reference to siloxen (I) and its derivatives. The degree of openness depends on the conditions of formation and subsequent treatment. The internal surface is determined from the adsorption isotherm; (I) is found to possess maximal subdivision, i.e., the whole material is accessible to the adsorptive. The H atoms in (I) can be replaced rapidly and quantitatively by halogens, OH, or NH₂. Chemical changes are sensitive to energy-liberating processes, e.g., the action of light, and many derivatives of (I) are coloured. Luminescence phenomena, which are common in oxidised (I), are described. Permutoid structures are inhomogeneous as regards composition and arrangement, and the concept of mols. cannot be applied. The importance of such structures in plant materials is pointed out.

R. H. F.

Selective adsorption of hydrocarbons and water vapour on alumina at atmospheric pressure. C. C. Ku, R. L. Huntington, and L. S. Reid (*Amer. Inst. Min. Met. Eng.*, 1943, *Tech. Paper* 1628, 13 pp.; *Petrol. Tech.*, 6, No. 7).—The adsorption of H₂O-hydrocarbon vapour mixtures by activated Al₂O₃ occurs in three stages. In the first both components are adsorbed and the ratio of one component to the other remains const. In the second phase H₂O vapour continues to

be adsorbed at the expense of adsorbed hydrocarbon which is desorbed. The third phase obtains when the Al_2O_3 is saturated with respect to both components. The adsorptive capacity of Al_2O_3 for hydrocarbon is reduced in presence of H_2O vapour although the adsorptive capacity for H_2O is not seriously affected by the presence of hydrocarbons. The data and theory presented are applied to several problems relating to the large-scale design and operation of plants for the dehydration of natural gas. C. R. H.

Relationship between energy of adsorption of a vapour on a solid and of immersion of the solid in a liquid. G. Jura and W. D. Harkins (*J. Chem. Physics*, 1943, 11, 561–562).—The heat of adsorption of a vapour on a solid can best be calc. from heats of immersion and condensation, but equations given in the literature for the relationship between these quantities are incorrect. A term involving heat of emersion of the solid and adsorbed vapour to form a clean surface should be subtracted from the usual expression. A. J. M.

Surface tension and activity of sulphur dioxide solutions of potassium thiocyanate. W. G. Eversole, T. F. Hart, and G. H. Wagner (*J. Physical Chem.*, 1943, 47, 703–709).—The surface tension (γ) at 15°, 20°, and 25° of dil. solutions of KCNS in liquid SO_2 has been determined. Activity coeffs. at the same temp. have been calc. from v.p. data. The plot of γ/γ_0 against mol. concns. gives vals. which agree with the Onsager-Samaras equation (A., 1934, 1068) only at infinite dilution. At higher concns. the observed vals. of γ/γ_0 are > the calc. vals. C. R. H.

Interfacial tension of sodium secondary alkyl sulphate solutions against oils. R. G. Aickin (*J. Soc. Dyers and Col.*, 1944, 60, 36–40).—Interfacial tensions of solutions of Na sec.-alkyl sulphates (I) against hydrocarbon and other oils at 20° fall with increasing concn. A sharp break in the smooth curve occurs at the crit. concn. of 0.95 g. per l. whatever the nature of the oil phase. Addition of electrolytes to (I) reduces the interfacial tension and crit. concn., this effect being due almost entirely to positive ions, although it is demonstrated that negative ions have a slight influence in certain concns. The results are explained on the basis of a long-chain ion being the surface-active entity. C. S. W.

Antonoff's rule. G. Antonoff (*J. Physical Chem.*, 1943, 47, 709–710).—A criticism of Yoffe and Heymann (cf. A., 1943, I, 276) and a defence of the rule. C. R. H.

Oil-water interface of mineral oil-polar compound mixtures. R. G. Aickin (*J. Soc. Dyers and Col.*, 1944, 60, 41–43).—Measurements of the interfacial tension between H_2O and various mixtures of mineral oil (I) with oleic acid, oleyl alcohol, and glyceryl mono-oleate (II) indicate the presence of a stable 1:1 (I)-polar compound complex over a wide range of concns., which explains the stability of emulsions stabilised by mixtures of oil-sol. and H_2O -sol. polar compounds. (II) reduces the interfacial tension of (I) against H_2O to a very low val. and is active at concns. >2 g. per l. Solutions of (II) in (I) are shown to be micellar. C. S. W.

Extension of attractive energy of a solid into an adjacent liquid or film and decrease of energy with distance. W. D. Harkins and G. Jura (*J. Chem. Physics*, 1943, 11, 560–561).—Experiments on the attractive energy between TiO_2 (in the form of anatase) and H_2O , and its variation with the thickness of the H_2O layer, indicate that films of N_2 at -195.8° , and of H_2O at 25° are multimol. on many solids at higher pressures. The layers of the above liquids under the temp. conditions stated are 7–10 mols. thick. A. J. M.

Flotation experiments with 8-hydroxyquinoline as collector. V. Flotation experiments on oxide-like compounds in the presence of metallic salts. H. Erlenmeyer, H. Kam, and W. Theilheimer (*Helv. Chim. Acta*, 1943, 26, 1129–1131).—Addition of various metallic salts produces marked and sp. effects on the flotation of various metallic oxides, etc. in presence of 8-hydroxyquinoline. Results with Fe_2O_3 , Cr_2O_3 , hæmatite, and chromite are tabulated. F. J. G.

Charge and stability of colloids. V. Potentiometric titrations of chromium hydroxide sol. VI. Absorption of precipitating and stabilising ions by As_2S_3 and $\text{Fe}(\text{OH})_3$ sols at their coagulating concentrations. B. P. Yadava (*J. Indian Chem. Soc.*, 1943, 20, 219–222, 223–226; cf. A., 1943, I, 256).—V. $\text{Cr}(\text{OH})_3$ sols give results corresponding with those found for $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$. The mechanism of the Cl^- release is attributed to electrical adsorption on the surface of the colloidal particles.

VI.—Direct measurements of the adsorption of both ions of an electrolyte by As_2S_3 and $\text{Fe}(\text{OH})_3$ during coagulation of their sols show that ions bearing the charge of the same sign as the sol are adsorbed to an extent that decreases with increasing valency of the coagulating ion. The mol. ratios of coagulating ions of different valency adsorbed during coagulation vary only slightly with the speed of coagulation, and differ greatly from the ratios of their reciprocal valencies. The abs. adsorption of coagulating ions decreases with increasing valency, although the relative adsorption increases. The above statements refer to the total amounts of adsorbed coagulating ions minus the amount equiv. to the adsorbed non-coagulating ion. F. G.

Dependence of viscosity of nitrocellulose solutions on the degree of esterification. H. A. Wannow (*Kolloid-Z.*, 1943, 102, 29–34).—Two celluloses were nitrated in five mixtures of H_3PO_4 - P_2O_5 - HNO_3 of varying HNO_3 content to give nitrocelluloses (I) of N content from 10.70 to 13.85%. The degree of polymerisation of (I) was found by osmotic pressure measurements to be closely similar throughout the series. The η of (I) in COMe_2 solution increased with N content of (I), extrapolated vals. of η_{sp}/c at $c \rightarrow 0$ ranging from 0.168 to 0.316 in one instance. The increase is attributed to greater solvation of the (I). R. H. F.

"Viscosation," molecular form, and solvation [of colloidal solutions]. Proposal for standardisation. H. Fromm (*Kolloid-Z.*, 1943, 102, 86–90).—The term "viscosation" is used to describe the increase of η with concn. Methods of expressing concn. are examined in relation to the change in size of solute particles arising from solvation. New terms and symbols are proposed for the principal magnitudes in η -concn. relationships. R. H. F.

pH measurements on thixotropic gel systems using the glass electrode. R. C. Vogel and M. W. Lisse (*J. Physical Chem.*, 1943, 47, 678–685).—The first gelation of three gel-forming substances [$\text{Fe}(\text{OH})_3$, $\text{Th}(\text{MoO}_4)_3$, and bentonite], their thixotropic liquefaction, and the re-gelation of the sols have been examined. In the primary gelation the bentonite system showed no pH change, whereas the pH of the $\text{Fe}(\text{OH})_3$ system decreased and the pH of the $\text{Th}(\text{MoO}_4)_3$ system increased. No pH changes were observed during the subsequent liquefactions and re-gelations. C. R. H.

Theory of genesis of fibres. I. W. Ostwald (*Kolloid-Z.*, 1943, 102, 35–60).—The general conditions determining formation of fibres of all types, natural and artificial, are discussed. A fibre can originate by translatory motion of a nuclear disc (solid fibre) or ring (hollow fibre), and can grow either basally or apically. It may result from any of the processes of condensation, deformation, dissolution, or partial dispersion. Five fundamental questions regarding the physico-chemical conditions necessary for fibre growth are considered in detail, viz., (1) processes providing material for the growing fibre, (2) transport mechanism making the material available at the right point, (3) energy-providing processes, (4) factors determining direction of growth, (5) formative mechanism controlling shape and size of fibres. The phenomena of growth of Ag fibres on heated Ag_2S and of Cu fibres on Cu.S are described in detail, and theories advanced which comply with the 5 conditions for growth. The Ag ions in heated Ag_2S are mobile and exert an ionic pressure on a particle of Ag in contact with the Ag_2S . This leads to deposition of Ag atoms, electronic equilibrium being maintained by volatilisation of S derived from S ions in the lattice. Many details of the phenomenon are in accordance with the theory. The electrochemical processes are different in Cu fibre formation. R. H. F.

Electrokinetic properties and surface conductivity of cellulose and oxycellulose, with reference to the carboxyl group content. G. Rabinov and E. Heymann (*J. Physical Chem.*, 1943, 47, 655–668).—Experimental conditions and theoretical considerations affecting the streaming-potential method of determining the ζ -potential of cellulose (I) are discussed. The samples examined were purified cottons, cotton wool, oxidised (I), mercerised (I), and regenerated (I). In distilled H_2O ζ decreases and surface conductivity (K) increases with increase in acid val. of (I). Partial substitution by Na or Ca of H in the CO_2H in (I) decreases ζ slightly and K considerably. The effect of electrolytes is generally to decrease ζ , but alkali chlorides increase ζ to a max. at $\sim 0.0001\text{N}$, above which concn. ζ decreases. This max. is not due to dispersion of K . K is increased by uni-univalent and bi-univalent electrolytes and reduced by electrolytes furnishing ter- and quadri-valent cations. Of two explanations to reconcile increase of K with simultaneous decrease in ζ , one assumes preferential anion adsorption on negatively charged surfaces, the other assumes that the parts of the double layer which determine ζ and those which determine K are not identical. C. R. H.

VI.—KINETIC THEORY. THERMODYNAMICS.

Attainment of thermal equilibrium between a gas and a hot surface. P. M. Doty (*J. Chem. Physics*, 1943, 11, 557–559).—Experimental data due to Bryce (A., 1937, I, 85) can be used to show that all the H. mols. reaching a hot W wire come to equilibrium and return to the gas phase as atoms and mols. in equilibrium concns. governed by the temp. of the wire and the no. of mols. striking it. This is not applicable generally to gases in contact with hot surfaces. Mols. which suffer only elastic collisions with the hot surface are not in contact long enough for the attainment of equilibrium. It is probable that complete thermal equilibrium is attained only for mols. and surfaces between which chemi-adsorption occurs. A. J. M.

Isomerisation equilibrium allene \rightleftharpoons methylacetylene. D. A. Frank-Kamenetzki and V. G. Markovitsch (*Acta Physicochim. U.R.S.S.*, 1942, 17, 308–313).—The vals. of the equilibrium const., calc. from spectroscopic and heat of hydrogenation data, are 15.6,

9.9, 5.5, 4.7, and 4.2 at 82°, 200°, 400°, 500°, and 600° respectively. With rise of temp. the proportion of $C(CH_3)_2$ in the equilibrium mixture rises from 8.0% to 19.2%. Revised vals. for the entropy of $C(CH_3)_2$ at these temp. are 60.92, 65.87, 73.44, 76.78, and 79.91 g.-cal. per degree per mol. respectively. C. R. H.

Transitions between homogeneous and heterogeneous systems. J. Stauff (*Z. Elektrochem.*, 1941, 47, 820).—If the state of aggregation is determined as a function of total concn. by means of the law of mass action, it is possible to distinguish between homogeneous and heterogeneous equilibria in colloid systems. The equilibrium between colloidal aggregates and single mols. has been investigated in the case of soaps by means of colour indicators. The colour change of the indicator is determined spectrophotometrically. When the aliphatic chain has 8, 10, or 12 C the equilibrium is homogeneous. A. J. M.

Thermodynamic dissociation constants of hydroxy- and alkoxybenzoic acids. B. Jones and J. C. Speakman (*J.C.S.*, 1944, 19—21).—Thermodynamic dissociation consts., measured at 20° by a potentiometric method, have been obtained for *o*-, *m*-, and *p*-OR-C₆H₄-CO₂H where R = H, Me, Et, Pr^α, and Pr^β and for *m*-OBu^α-C₆H₄-CO₂H. Where R = H or Me, *pK* increases in the order *o* < *m* < *p*, but where R = Et, Pr^α, or Pr^β the order is *m* < *o* < *p*. The influence of the size of R on *pK* varies with the position of the substituent in the nucleus. For *o*-compounds *pK* increases in the order H < Me < Et < Pr^α = Pr^β, but for *m*- and *p*-compounds the change in *pK* as R increases from H to Pr^β is irregular. The data are discussed with reference to existing theories of the effect of substituents in C₆H₄ compounds. C. R. H.

Raman spectra of some complex halides of mercury. M. R. Nayar and J. R. Saraf (*J. Indian Chem. Soc.*, 1943, 20, 312—314).—Raman frequencies of mixed solutions of K and Hg^{II} halides afford evidence of the existence in solution of the ions HgCl₃⁺, HgCl₂⁰, HgBr₂⁰, and HgI₂⁰. The characteristic frequencies are 300, 274, 172, and 126 cm.⁻¹. The data favour the view that equimol. mixtures of HgCl₂ and KCl form KHgCl₃ in solution. Solubility difficulties prevented evidence being obtained for the formation of KHgBr₃ and KHgI₃ in solution. C. R. H.

Thermodynamics of polar-non-polar solutions. H. Hartmann (*Z. Elektrochem.*, 1941, 47, 856—858).—It is assumed that in a solution of polar mols. in a non-polar solvent, there is a statistical mol. atm. of dipolar mols. similar to the atm. of ions in strong electrolytes. Quant. treatment leads to no contradiction of experimental thermodynamic results. The view adopted gives a better explanation of dependence of concn. on f.p. depression. A. J. M.

Inter-relation of oxygen pressure, temperature, and composition in the system Fe₃O₄-Fe₂O₃. N. G. Schmahl (*Z. Elektrochem.*, 1941, 47, 821—836).—The relation between O. pressure (*p*), temp., and composition in the above system has been investigated over the range 1290—1410°. The decomp. pressure over a known mass of oxide was determined at const. temp., after which a definite quantity of O₂ was withdrawn, and the decomp. pressure again determined. A univariant equilibrium exists over a certain range of compositions near the pure oxides. It varies with temp. according to the reaction isochore. The heat of the reaction 4Fe₃O₄ + O₂ = 6Fe₂O₃ is calc. to be 124.3 kg.-cal., a val. which differs only slightly from that obtained by direct determinations at room temp. An equilibrium diagram is given (1100—1800°) including two isobars at *p* = 159 and 760 mm. A. J. M.

Binary system NaPO₃-Na₂P₂O₇. G. W. Morey and E. Ingerson (*Amer. J. Sci.*, 1944, 242, 1—6).—The work of Partridge *et al.* (*A.*, 1941, I, 211) is, in general, confirmed. Phase equilibrium data and the phase diagram reproduced show that there is a eutectic at 552° and 0.31 wt.-fraction Na₂P₂O₇, at which the cryst. phases are NaPO₃ and Na₅P₃O₁₀, the only binary compound between the two end members. Na₅P₃O₁₀ melts incongruently at 622°, forming crystals of Na₄P₂O₇ and liquid containing 0.495 wt.-fraction Na₂P₂O₇. Optical properties of these three compounds are recorded. L. S. T.

Nature of the difference in the character of the phase diagrams of the higher fatty acids and corresponding triglycerides. G. B. Ravitsch and V. A. Volnova (*Acta Physicochim. U.R.S.S.*, 1942, 17, 323—336).—Various physical properties of the systems stearic acid-palmitic acid and tristearin-tripalmitin have been examined and the phase diagrams of the systems have been compared. In the acid system a mol. compound is formed giving limited solid solutions with both acids. If it is assumed that it is the H bond which enables mol. compounds to be formed, then the absence of CO₂H groups in the triglyceride systems explains why a similar mol. compound is not formed in this system. On the other hand continuous solid solutions are formed which disintegrate with time as a result of the transformation of one of the triglycerides into a more stable form with a higher m.p. C. R. H.

Phase boundaries in ternary systems of sodium oleate, compared with other soaps. J. W. McBain, R. D. Vold, and K. Gardiner (*Oil and Soap*, 1943, 20, 221—223).—The boundaries of the region of

isotropic solution have been determined for freshly made solutions of Na oleate (I) in H₂O containing NaCl at 90° and 100° (cf. Vold, *A.*, 1940, I, 112). Prolonged heating in glass tubes alters solutions of (I), rendering the soap less sol. (*θ*₁ increases), apparently owing to instability of the soap itself rather than to reaction with glass. When Na silicate replaces NaCl, (I) is not salted out, but the solution tends to set to a clear jelly on cooling. Existing published data for the boundaries of isotropic solution of six individual pure soaps [Na and K laurate, Na palmitate and stearate, and (I) and K oleate] and the Na soaps of tallow, olive, and coconut oils in H₂O containing salt at 90° and other temp., have been collated and the curves redrawn to the same scale for comparison. *θ*₂ (temp. of ready solubility, cf. McBain, *et al.*, B., 1941, II, 390) for these and other commercial soaps are tabulated. In spite of its high solubility in H₂O, (I) is almost as readily salted out by NaCl as is the stearate. The binary diagram found for pure (I) in H₂O (*θ*₁ and *θ*₂ curves) is compared with the picture obtained for systems containing small amounts of NaCl (1.5% of the oleate present) such as are met with in commercial soap boiling. E. L.

Polytherm of the ternary system: sodium chloride-sodium bromide-water from complete f.p. to 50°. N. A. Vlasov and A. G. Bergman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 211—214).—Solubilities of NaBr and NaCl in H₂O are recorded for -20° to 50°. In this temp. range there are two fields of solid solutions, one consisting of the anhyd. salts, the other of the dihydrates. The fields of crystallisation of ice, Na(Cl,Br)·2H₂O, and Na(Cl,Br)·5H₂O meet in a eutectic point at -29.2° with NaCl 6.0, NaBr 31.6, H₂O 62.4%. F. R. G.

Fusibility diagram of the ternary system sodium chloride-fluoride-chromate. I. S. Rasnonskaja and A. G. Bergman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 176—177).—In a study of baths for thermal treatment of metals, heat carriers, and welding fluxes, the ternary and the three component binary systems were investigated. NaCl-NaF has m.p. 675° (33.5 mol.-% NaF); NaCl-Na₂CrO₄ has m.p. 572° (78.5 mol.-% Na₂CrO₄); NaF-Na₂CrO₄ has m.p. 642° (81.5 mol.-% Na₂CrO₄); all are simple eutectics. The eutectic point of the ternary system is at 526° and NaF 13, NaCl 21.5, Na₂CrO₄ 65.5 mol.-%. N. M. B.

Ternary systems barium chloride-dioxan-water and calcium chloride-dioxan-water. H. F. Bogardus and C. C. Lynch (*J. Physical Chem.*, 1943, 47, 650—654).—Data for the 25° isotherm for both systems are presented in tabular and triangular diagrammatic form. The solvate, CaCl₂·C₄H₈O₂·2H₂O, has been isolated. C. R. H.

Sulphate nitrophoska. I. Polytherm of the ternary system H₂O-K₂SO₄-(NH₄)₂SO₄. A. G. Bergman and M. L. Schelochovitch (*J. Appl. Chem. Russ.*, 1942, 15, 187—193).—The eutectic point for the H₂O-K₂SO₄ system is at 6.5 wt.-% of K₂SO₄ and -1.6°, and for H₂O and (NH₄)₂SO₄ at 39.6 wt.-% of (NH₄)₂SO₄ and -18.86°. (NH₄)₂SO₄ and K₂SO₄ form a complete series of solid solutions between the f.p. and 30° (no measurements above 30°). J. J. B.

Simplest inorganic glasses on the basis of calcium nitrate. A. G. Bergman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 304—306).—In the system Ca(NO₃)₂-KNO₃-NaNO₃ glasses are obtained by the solidification of melts in the field of primary crystallisation of 4KNO₃·Ca(NO₃)₂ and adjoining regions. The eutectic is at 133° and the ternary transition point is at 160° and 53.9% KNO₃, 29.4% Ca(NO₃)₂. The system Ca(NO₃)₂-NaNO₃ has a eutectic at 232° and 54.9% of NaNO₃, with no compound formation. The system Sr(NO₃)₂-KNO₃-NaNO₃ shows neither glass nor compound formation. L. J. J.

Heat of formation of sodium aluminate solution and of cryolite. W. A. Roth (*Z. Elektrochem.*, 1941, 47, 813).—A preliminary note reporting thermochemical determinations with Na aluminate solution and Na₂AlF₆. The solubility of Na₂AlF₆ and the sp. heat and electrical conductivity of its solutions have also been determined. No numerical data are given. A. J. M.

Enthalpy and heats of dilution of the system HCl-H₂O. C. C. Van Nuys (*Trans. Amer. Inst. Chem. Eng.*, 1943, 39, 663—678).—The thermal properties of the system are represented on two charts, which enable direct determination of the heat changes in any interaction of HCl and H₂O to be made. F. Rb.

High-temperature heat content of calcium carbide. G. E. Moore (*Ind. Eng. Chem.*, 1943, 35, 1292—1294).—The heat content of CaC₂ (purity 91%) has been measured at 200—1000°, and the results corr. for the major impurities. A transition occurs at 447° ± 5° with Δ*H* = 1330 g.-cal. per g.-mol. *C_p* = 16.40 + 2.84 × 10⁻³*T* - 2.07 × 10⁻⁶*T*² at 25—447° and 15.40 + 2.00 × 10⁻³*T* at >447°. J. W. S.

VII.—ELECTROCHEMISTRY.

Electrical resistance of dilute alloys of copper, silver, and gold. J. O. Linde (*Metalwirts.*, 1941, 20, 1140—1141).—The resistance and pressure coeff. of resistance of a no. of alloys of Cu, Ag, and Au

have been determined. The regularity of the results gives an indication of the condition of the outer electrons of the atoms going into solid solution. It is considered that with dissolved elements which have an outer electron configuration of the inert-gas type when in the free gas condition, the same configuration will often be formed in the dil. solid solution. The theoretical discussion of the regularity of the results is in agreement with Mott's views.

C. I. H.
Hydrogen bonds and electrolytic conduction. P. Wulfi and H. Hartmann (*Z. Elektrochem.*, 1941, 47, 858—867).—Hückel's theory of proton conduction in H_2O is examined. The mobility of H^+ in dioxan- H_2O mixtures was investigated, but no inference concerning the accuracy of Hückel's view could be made. Diffusion of H^+ in acids does not agree with Hückel's theory. The theory that the high mobility of H^+ and OH^- is due to the formation of exchange bridges of the type $\begin{pmatrix} H & OH & OH & H \\ | & | & | & | \\ H & H & H & H \end{pmatrix}$ or $\begin{pmatrix} OH & H & OH & H \\ | & | & | & | \\ H & H & H & H \end{pmatrix}$, produced

by polar association of OH groups with H bonds, is proposed. This is in agreement with the small temp. coeffs. of the mobilities of these ions, and gives a reasonable explanation of the effect of pressure on conductivity of acids and bases.
 A. J. M.

Electro-dialysis in a two-chamber cell. G. Untermann (*Z. Elektrochem.*, 1941, 47, 876—879).—If a cell, separated into an anode and cathode compartment by a diaphragm, is filled with a dil. acid, a stationary state is set up. Only H^+ ions migrate through the diaphragm. The concn. change in the diaphragm is linear, and is an exponential function of potential. The potential at the diaphragm is very small for the concns. involved. The current intensity is \propto concn. difference between anode and cathode compartments, and inversely \propto thickness of diaphragm. The concn. of electrolyte (C_x) in the cathode compartment when the cell is filled with acid can be calc. from the formula $C_x = C_0(4RTL\gamma/EFd)(u_H''/u_A' + u_A'') = 1 - \sqrt{1 - (i/i_0)}$ where C_0 = initial concn., E = terminal voltage, L = half electrode distance, d = thickness of diaphragm, γ = free cross-section in the diaphragm for the solution, u_H'' = mobility of H^+ in diaphragm, u_H' , u_A' = mobilities of ions in H_2O , i = final current, i_0 = initial current. A similar formula holds for the concn. in the anode compartment when the cell is filled with a base.

A. J. M.
Contact potentials at water phases of meteorological interest. E. Lange (*Z. Elektrochem.*, 1941, 47, 867—876).—In order to investigate the origin of atm. electricity, the contact potentials at the surfaces of the various H_2O phases have been determined. The ionisation method was used for H_2O phases in damp air. For the system fresh hoar-frost/ice, a contact potential of -0.30 v. was found in air. The val. depends on temp., frost and ice at temp. $> -10^\circ$ giving no marked potential. For the system H_2O /ice in air a potential of -0.10 v. was obtained. The effect of impurities was investigated. Metals have a positive potential against H_2O in air, but in contact with a plane ice surface they have a negative potential.

A. J. M.
Theory of concentration polarisation. B. Levitsch (*Acta Physicochim. U.R.S.S.*, 1942, 17, 257—307).—Mathematical. The influence of electrode rotation, electrode shape, and stirring of the electrolyte on the rate of supply of ions to the electrode has been investigated and satisfactorily applied to available data.
 C. R. H.

Relation between metal overvoltage and activity of added organic substances in electrolytic deposition of metals. H. Fischer and J. Goesch (*Z. Elektrochem.*, 1941, 47, 879—889).—Addition of alkylamines to $CuSO_4$ solution causes an increase in the potential of separation of Cu with free acid present. The increase of potential rises with increasing concn. of the added substance. The larger is the added mol. the greater is the increase of potential, but isomeric amines may produce different effects. The magnitude of the increase and the form of the potential-time curve are dependent on the concn. of acid in the electrolyte in the case of many amines. The potential rise is usually not permanent, but has a marked effect on the nature of the deposit. For overvoltages > 30 mv. finer-grained deposits are formed.
 A. J. M.

VIII.—REACTIONS.

Limits of inflammability and ignition temperatures of acetic anhydride. G. W. Jones, F. E. Scott, and B. S. Scott (*U.S. Bur. Mines*, 1943, *Rept. Invest.* 3741, 5 pp.).—The temp. between which air saturated with Ac_2O forms inflammable mixtures are 47.3° and 74.4° , the respective concns. of Ac_2O being 2.67 and 10.13 vol.-%. The flash point of Ac_2O determined in a Tag closed-cup tester is 51° , and the ignition temp. in air and O_2 are 392° and 361° respectively.
 C. R. H.

Kinetics of consecutive reactions consisting of bimolecular and unimolecular stages. A. A. Balandin and L. S. Leibenson (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 22—24).—The equations for consecutive reactions of the type $2A \rightarrow B \rightarrow C$ are solved, and the results compared with experiment in the case of the formation of CH_4 from equimol. mixtures of $NaOAc$ and $NaOH$. The reaction is made up of two consecutive ones. The first, the formation of an

intermediate compound, is bimol., and has a velocity coeff. that of the unimol. conversion of the intermediate compound into the final products. The concn. of the intermediate compound is small.

A. J. M.
Ether-like compounds. VII. Action of chlorine atoms on the velocity of the spontaneous hydrolysis of esters by water. E. J. Salmi and T. Suonpää (*Ber.*, 1940, 73, [B], 1126—1131; cf. A., 1940, II, 64).—Relative k_w for hydrolysis of $CCl_3 \cdot CO_2R$ at 25° in H_2O or 50% dioxan are $R = Me$ 480, Et 100, $[CH_3]_2 \cdot OMe$ 275, and $[CH_3]_2 \cdot Cl$ 796 (cf. A., 1939, I, 327). For $CCl_3 \cdot CH_2 \cdot OAcyl$ at 35° are $acyl = CH_3 \cdot Cl \cdot CO$ 0.0000431 and $CHCl_2 \cdot CO$ 0.00302, and k_a at 35° are $acyl = Ac$ 0.00384, $CH_3 \cdot Cl \cdot CO$ 0.00853, and $CHCl_2 \cdot CO$ 0.0314.

For compounds, $CRR' < \begin{pmatrix} CO \\ | \\ O \end{pmatrix} > CH \cdot CCl_3$ relative are $R = R' = H$ 237, $R = H$ and $R' = Me$ 100, $R = R' = Me$ 8.02, and $R = Me$ and $R' = Et$ 2.23; corresponding vals. for k_a at 25° are 169, 100, 9.45, and 2.93, respectively.
 R. S. C.

Catalytic action of natural mineral waters. II. G. Cronheim (*J. Physical Chem.*, 1943, 47, 638—645; cf. A., 1941, I, 214).—The catalytic oxidation of HCO_2H by H_2O_2 and natural mineral waters (M) from Saratoga Springs has been studied. Oxidation is complete in presence of H_2O_2 and M , but in absence of M oxidation is very slow. Fe^{++} ions are necessary for catalysis but their concn. is of secondary importance. The rate of oxidation depends on $[H_2O_2]$. The rise in pH due to removal of HCO_2H increases the dissociation of H_2O_2 and the HO_2^{\cdot} formed reduces Fe^{+++} to Fe^{++} which are necessary for catalysis. Cu^{++} , Mn^{++} , and to a small extent Pd^{++} ions accelerate oxidation by influencing the oxidation-reduction equilibrium of Fe ions.
 C. R. H.

Effect of temperature on rate of hydrolysis of triglycerides by pancreatic lipase.—See A., 1944, III, 284.

Catalysis of the liquid-phase stage of coal hydrogenation.—See B., 1944, I, 88.

Electrochemical oxidation of nickel hydroxide. N. P. Fedoteev and V. V. Svetschnikova (*J. Appl. Chem. Russ.*, 1942, 15, 105—119).—The best conditions for electrochemical oxidation of an aq. suspension of NiO in a one-compartment cell are: ~ 28 g. of NiO per l., $[NaCl] \geq 5N$, $[NaOH] = 0.025N$, 16 amp. per l. of electrolyte, cathodic c.d. 0.075 amp. per sq. cm., anodic c.d. 0.1—1 amp. per sq. cm., the electrodes being of graphite. The black hydrate (I) obtained contains 1.71 O per l Ni atom; the energy consumption is 20—30 kw.-hr. per 1 kg. of active O. A similar hydrate can be prepared by electrolysis $5N$ - $NaCl$ between a Ni and a graphite anode and a Ni cathode but the energy consumption is higher since a large fraction of the OCI^{\cdot} produced is decomposed before meeting a particle of NiO ; the ratio O:Ni in this hydrate is ≤ 1.7 . (I) can be used for pptg. Co^{++} from the $NiSO_4$ baths for Ni refining in the same way as black hydrate manufactured by chemical oxidation with $NaOCl$. The electrochemical oxidation is more economical.
 J. J. B.

Electrolytic oxidation of thiosulphate [ions] in ethylene glycol solution.—See B., 1944, I, 98.

Alloy [electro]deposition.—See B., 1944, I, 111.

Quantitative effect of X-rays on ascorbic acid in simple solution and in mixtures of naturally occurring compounds.—See A., 1944, III, 284.

Photo-reduction of ferric chloride in aqueous solutions in presence of organic acids and sugars. P. R. Bavdekar (*J. Univ. Bombay*, 1943, 12, A, Part 3, 47—56).—The photochemical reduction of $FeCl_3$ in presence of $H_2C_2O_4$, citric or tartaric acid, glucose, sucrose, or fructose is of zero order. The temp. coeff. over the range 30 — 40° is ~ 1.2 . The rate of reduction increases with decreasing λ , and \propto the intensity of the incident radiation, but the quantum efficiency at 35° is < 0.5 under the most favourable conditions studied ($0.05M$ - $FeCl_3$ in presence of $H_2C_2O_4$ and with 4725 Å radiation).

Action of ultra-violet light on liquid benzene.—See A., 1944, II, 93.

Splitting of sucrose by ultrasound. I. L. Roitsch and A. S. Starkerman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 10—12).—The inversion of sucrose (I) by ultrasonic waves formerly reported (cf. Sokolov, A., 1936, 1077) may be due to changes of temp. The effect of temp. on the rate of inversion of (I) in acid solution has been investigated. The rate increases considerably with rise of temp. The effect of ultrasonic waves on the inversion has also been investigated, both in presence and in absence of acid, and with strict temp. control. In absence of acid, no change in the optical rotation of the solution was observed, and in solutions of (I) in dil. HNO_3 , the variation of the rotation with time was identical in a sample which had been exposed to ultrasonic waves, and in another which had not. Hence ultrasonic waves of the intensity (0.25 w. per sq. cm.) and frequency (6×10^7) used have no effect on the inversion of (I).
 A. J. M.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Separation of molecules of equal masses in a separation tube. K. Clusius and H. Kowalski (*Z. Elektrochem.*, 1941, 47, 819).— C_2H_2 , CO_2 , and $He-D_2$ mixtures have been separated by a separation tube, the C_2H_2 and D_2 appearing on the "heavy" side. Pure D_2 has also been separated from H_2 -HD mixtures. A. J. M.

Properties and dihydrate of lithium bromate. I. N. Averko-Antonovitch (*J. Gen. Chem. Russ.*, 1943, 13, 267—270).— ρ and η of aq. solutions containing 10—52% of $LiBrO_3$ (I) are given; at 0°, the saturated solution contains 61.2% and at 20°, 64.5% of (I). At room temp., (I) readily forms supersaturated solutions from which the metastable phase [anhyd. (I)] separates; it forms pyramidal crystals consisting of fine aggregates in which the crystallites are short prisms with high n , strong double refraction, and straight extinction. $LiBrO_3 \cdot H_2O$ (II) separates from almost saturated solutions after seeding, in long thin rhomboidal plates having similar optical properties to (I); at 110°, (II) loses H_2O without melting. The dihydrate, $LiBrO_3 \cdot 2H_2O$ (III), was isolated from the crystals deposited at $\sim 50^\circ$ from a solution saturated at room temp. (III) forms short or flat prisms with optical properties similar to (I), melts in its H_2O of crystallisation at 60°—70° and loses all H_2O at 110°. This observation provides some evidence that, near the eutectic point (-47°), (I) crystallises as (III). R. C. P.

Complex compounds of diguanide with bivalent metals. VII. Copper, nickel and cobalt(ous) ethylenedibis(diguanide) salts. Cobaltous diguanidinium sulphate and hydroxide. P. Ray and S. P. Ghosh (*J. Indian Chem. Soc.*, 1943, 20, 291—297).— $(CH_2 \cdot NH_2)_2 \cdot 2HCl$ and dicyanodiamide (1 mol.) are fused at 140—150°, and the filtered aq. extract is pptd. with $CuSO_4$, to give the complex sulphate, (I), $[CuE \cdot H^+]_2[SO_4]_2 \cdot 4H_2O$, almost insol. in H_2O , stable to dil. but not conc. acids; the formula (I) is suggested for the complex. Digestion with $NaOH$ affords the crude complex hydroxide, from which and the appropriate NH_4 salt the following salts are obtained: $[CuE \cdot H^+]_2[Cl]_2 \cdot 1.5H_2O$ (II); $[CuE \cdot H^+]_2[Br]_2 \cdot 1.5H_2O$; $[CuE \cdot H^+]_2[I]_2 \cdot 1.5H_2O$; $[CuE \cdot H^+]_2[NO_3]_2 \cdot 1.5H_2O$. The following salts are obtained from (II) and Na or K salts: $[CuE \cdot H^+]_2[S_2O_3]_2 \cdot 2.5H_2O$; $[CuE \cdot H^+]_2[SCN]_2 \cdot 1.5H_2O$; $[CuE \cdot H^+]_2[NO_2]_2 \cdot 1.25H_2O$; the base, $[CuE] \cdot H_2O$, is pptd. from (II) by dil. NH_3 . The prep. of the Ni complex salts, $[NiE \cdot H^+]_2[SO_4]_2 \cdot H_2O$ and $[NiE \cdot H^+]_2[Cl]_2 \cdot 1.5H_2O$ (III), is analogous to that of (I), whilst the following salts are obtained from (III): $[NiE \cdot H^+]_2[Br]_2 \cdot 2.5H_2O$; $[NiE \cdot H^+]_2[I]_2 \cdot 1.5H_2O$; $[NiE \cdot H^+]_2[S_2O_3]_2 \cdot 2.5H_2O$; $[NiE \cdot H^+]_2[CNS]_2 \cdot 1.5H_2O$; $[NiE \cdot H^+]_2[NO_2]_2 \cdot 1.5H_2O$; $[NiE \cdot H^+]_2[NO_3]_2 \cdot 1.5H_2O$; the base, $[NiE]$, is only obtainable impure [by pptg. (III) with either dil. $NaOH$ or NH_3]. The equiv. mobility of $[CuE \cdot H^+]$ is 49.6 at 32°, and of $[NiE \cdot H^+]$ 50.72 at 34°. Ethylenedibis(diguanide) sulphate (2 mols.) in dil. NH_3 and Ni-free $CoCl_2 \cdot 6H_2O$ afford a yellow ppt. of $[CoE \cdot H^+]_2[SO_4]_2 \cdot 2.5H_2O$, which gives a violet solution of a hydroxo-aquocobaltic complex in $BaCl_2$ or boiling H_2O . With very dil. $NaOH$, it gives impure base, $[CoE]$, but with NH_3 it gives a red solution containing Co^{+++} . No other salts can be prepared. From diguanide sulphate, $[CoD_2 \cdot H^+]_2[SO_4]_2 \cdot 4H_2O$ is prepared analogously, and is dehydrated at 105° in N_2 to $[CoD_2 \cdot H^+]_2[SO_4]_2$. The moist base, $[CoD_2 \cdot H^+]_2(OH)_2$, slowly oxidises in air to $[CoD_2 \cdot H^+]_2(OH)_3$ and $Co(OH)_3$, and in boiling H_2O gives a violet hydroxo-aquocobaltic bis(diguanide) complex; the anhydro-base, $[Co \cdot D_2]$ is formed at 70°. S. A. M.

Equilibrium reactions important for chemical analysis. N. A. Tananaev and R. A. Lovi (*J. Appl. Chem. Russ.*, 1942, 15, 214—222).— Ag_3PO_4 is transformed (99.8%) into $AgCl$ by 0.1N- $NaCl$; the reverse reaction $3AgCl + Na_3PO_4 \rightarrow Ag_3PO_4$ leads to the same equilibrium. Similarly, Ag_3AsO_4 is transformed into $AgCl$, $MgNH_4PO_4$ into Ag_3PO_4 (by $AgNO_3$) and $Pb_3(PO_4)_2$ (by $Pb(NO_3)_2$), and $Mg(OH)_2$ into $AgOH$ (by $AgNO_3$). (See also C., 1944, Part 2.) J. B.

Normal beryllium tungstate. V. I. Spitzin and V. I. Schostak (*J. Gen. Chem. Russ.*, 1943, 13, 279—285).— $BeWO_4 \cdot 3H_2O$ (I) was obtained as a pale yellow viscous mass by prolonged interaction in aq. suspension at room temp. of $Be(OH)_2$ (II) and H_2WO_4 (III); its properties suggest a non-ionised structure $[Be(H_2O)_3(WO_4)]$. Over P_2O_5 , (I) is converted into $BeWO_4 \cdot 2H_2O$. On heating, gradual dehydration of (I) occurs with rise of temp.; loss of the last mol. of H_2O begins above 250° and is accompanied by dissociation into BeO and WO_3 . Aq. solutions of $BeSO_4$ and Na_2WO_4 interact with formation of basic Be tungstates; (II) and (III) when boiled together in aq. suspension yield small amounts of sol. complexes in which $BeO : WO_3$ approximates to 1 : 1.5. R. C. P.

Low-temperature yellow zinc silicate phosphor. H. C. Froelich (*J. Physical Chem.*, 1943, 47, 669—677).—Yellow Zn_2SiO_4 phosphors have been prepared by heating (800—850°) a mixture of ZnO , SiO_2 , and preformed $MnSiO_3$ in steam and in absence of O_2 . The $MnSiO_3$ is prepared by heating $MnCO_3$ or MnO with SiO_2 in steam and H_2 at 800—850°. The primary reaction product is an amorphous Z (A., 1.)

orthosilicate complex which crystallises at $>775^\circ$. The Mn is present either as MnO or a Mn^{II} silicate, and reduction of Mn_2O_3 to MnO appears to be necessary. Phosphor formation probably proceeds thus: $2ZnO + Mn_2O_3 + (n+1)SiO_2 \rightarrow nZn_2SiO_4 \cdot Mn_2SiO_4 + 4O_2$, where $n \gg 1$. ZnO or Zn_2SiO_4 evidently catalyses the reduction of Mn_2O_3 . Rooksby and McKeag's interpretation (cf. A., 1941, I, 343) of the low-temp. forms of yellow Zn_2SiO_4 is erroneous. C. R. H.

Dehydration of mirabilite by a mixture of sodium and potassium chlorides.—See B., 1944, I, 133.

Chemistry and morphology of the basic salts of bivalent metals. XII. Cadmium hydroxyfluorides. XIII. Zinc hydroxyfluorides. W. Feitknecht and H. Bucher (*Helv. Chim. Acta*, 1943, 26, 2177—2195, 2196—2204).—XII. Basic Cd fluorides were prepared in three ways: (a) incomplete pptn. of aq. CdF_2 with alkali, (b) reaction of $Cd(OH)_2$ with aq. CdF_2 , and (c) reaction of CdO with NH_4F . From method (a) there is first obtained an unstable hydroxyfluoride III $[CdF_2 \cdot 2-9Cd(OH)_2]$, which in solutions containing excess of CdF_2 changes rapidly into hydroxyfluoride I $[CdOHF]$. III is more stable in alkaline solution, but slowly changes to hydroxyfluoride II $[CdF_2 \cdot 4-6Cd(OH)_2]$. I has a solubility product $\{[Cd^{++}] \times [OH^-] \times [F^-]\}$ of 2.2×10^{-10} . By method (c) large rhombic crystals are obtained. It has a lattice containing 6-co-ordinate Cd. II has a layer lattice structure similar to the hydroxide. III has a B_8 type lattice, in which only half the spaces available for the Cd are filled.

XIII. Basic Zn fluorides were obtained by pptn. of aq. ZnF_2 with aq. $NaOH$ and allowing the ppts. to age. Hydroxyfluoride I has a formula $ZnOHF$ although some of the F^- ions can be replaced by OH^- ions. It is stable only to small Zn^{++} concns. and has a lattice containing 4-co-ordinate Zn. Hydroxyfluoride II $[4Zn(OH)_2 \cdot ZnF_2]$ is stable only over a very small concn. range. It has a double layer lattice like the corresponding hydroxychloride. Hydroxyfluoride III has an ideal formula $[Zn(OH)_2 \cdot F_2]$. It has a C_8 type lattice; replacement of some of the F^- ions by OH^- ions increases the disarrangement observed. The basic fluorides of Zn are compared with those of Cd. J. F. H.

Reaction of niobium pentoxide with sodium hydroxide. I. V. I. Spitzin and A. V. Lapitzki (*J. Appl. Chem. Russ.*, 1942, 15, 194—203).—Even after being heated at 1000° Nb_2O_5 reacts with $N-4N-NaOH$ on a H_2O -bath or with molten $NaOH$ at 650°. After dissolving the reaction product in H_2O the salt $Na_4[Nb_5O_{15}O_3] \cdot 32H_2O$ (I) is formed. It is sol. in H_2O (1.6 g. in 100 c.c. of solution at 20°) but the solubility is much lowered by $NaOH$ (at 90° 0.11 g. in $N-NaOH$, 2.6 g. in H_2O). $NaNbO_3$ after being heated at 1000° is not attacked by boiling 5—40% $NaOH$; it cannot be an intermediate product in the alkaline dissolution of Nb_2O_5 . With $NaOH$, $NaNbO_3 \cdot 3.5H_2O$ easily affords (I). (See also C., 1944, Part 2.) J. J. B.

Sulphur monoxide. N. M. Emanuel (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 145—149).—The part played by SO as an intermediate in the oxidation of H_2S has been studied by examination of the influence of synthetic SO on the induction period of the reaction and on the explosion limits. Results confirm the view previously advanced by the author from the absorption spectra data (A., 1941, I, 217) that SO is the chief active intermediate product in the oxidation reaction. J. O'M.-B.

Complex compounds of rhenium. V. V. Lebedinski and B. N. Ivanov-Emin (*J. Gen. Chem. Russ.*, 1943, 13, 253—265).—No stable complexes are formed on treating K_2ReCl_6 (I) or K_2ReCl_5 (II) with NH_3 , C_2H_5N , or $CS(NH_2)_2$ in aq. solution. In anhyd. NH_3 , (I) and (II) partly dissolved, giving orange and yellowish-green solutions respectively, but no complexes were isolated. Saturated aq. solutions of (I) or (II) with a large excess of $(CH_2 \cdot NH_2)_2 \cdot H_2O$ give the compound $[ReO_2en_2]Cl$ (III), crystallising in yellow prisms. (III) with aq. KI gives the yellow crystalline iodide, $[ReO_2en_2]I$, and similarly, the sparingly sol. chlorate, picrate, platinichloride, and cobaltinitrile. Addition of HCl to aq. (III) (pH 5—6) gives a red coloration at pH 2.8—3.2, violet at HCl concn. 2.5 N., and deep blue at 8 N., the change being reversible on addition of alkali. From the red solution, the compound $[ReO(OH)en_2]Cl_2$ (IV) may be pptd. with $EtOH$; the corresponding cream-coloured platinichloride $[ReO(OH)en_2][PtCl_6]$ and dark red iodide $[ReO(OH)en_2]I_2$ may be pptd. from aq. solutions of (IV). Evaporation at room temp. of the blue solution or pptn. with $EtOH$ gives pale blue needles of the compound $[Re(OH)_2en_2]Cl_2$ (V). Heating (V) with conc. HCl gives a green crystalline substance of unknown composition. R. C. P.

Periodates of cobalt and nickel. R. K. Bahl, S. Singh, and N. K. Bali (*J. Indian Chem. Soc.*, 1943, 20, 227—228).—The following periodates have been prepared: $3CoO_2 \cdot Co(IO_3)_2 \cdot 10H_2O$; $Co_4I_2O_{11} \cdot 12H_2O$; $Ni_3(IO_6)_2 \cdot 13H_2O$, and $7NiO \cdot 2I_2O_7 \cdot 25H_2O$. F. R. G.

Iridium sulphito-chlorides. V. V. Lebedinski and M. M. Gurin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 128—130; cf. A., 1943, I, 97).—In the filtrate from the isolation of $Na_2Ir(SO_3)_4 \cdot 7H_2O$ O are formed yellow crystals of $Na_2Ir(SO_3)_4 \cdot Cl_2 \cdot 7H_2O$ (I), and, on further heating the solution, the $5H_2O$ salt (II). (I) is almost insol. in H_2O

and loses $7\text{H}_2\text{O}$ at 100° ; the dry salt is stable and is not decomposed at 250° . (II) loses 4 H_2O at 100° and the remaining H_2O at 170° ; the salt is stable and does not decompose below 300° . On heating (II) in an aq. solution of H_2SO_4 , transparent cryst. plates (III) separated after cooling; the reaction was $(\text{II}) + \text{H}_2\text{SO}_4 \rightarrow \text{Na} \cdot \text{H} \cdot \text{Ir}(\text{SO}_3)_4\text{Cl}_2 + \text{Na}_2\text{SO}_3$. The properties of (III), which crystallises with $10\text{H}_2\text{O}$, are discussed. N. M. B.

Preparation of monohydroxo-derivatives of quadrivalent platinum. A. A. Grunberg and L. J. Michelis (*Comp. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 209—210).— HOCl with K_2PtCl_4 yields $\text{K}_2[\text{PtCl}_4](\text{OH})\text{Cl}$; with *cis*- and *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ yields $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2](\text{OH})\text{Cl}$; with $[\text{Pt}(\text{NH}_3)_4]\text{Cl}$, yields mainly $[\text{Pt}(\text{NH}_3)_4\text{OHCl}]\text{Cl}_2$; and with $[\text{Pt}(\text{NH}_3)_4]\text{SO}_4$ yields $[\text{Pt}(\text{NH}_3)_4\text{OHCl}]\text{SO}_4$. F. R. G.

XI.—GEOCHEMISTRY.

Content of radon in the waters of the Tartar autonomous S.S.R. V. Tscherdintzev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 206—208).—The average content of Rn in waters in the region of Cristopol is low, probably owing to the well-preserved tectonic structure of the rocks which, accordingly, show low emanating powers. L. S. T.

Sulphide waters of the Permian of the Polasna-Krasnokamsk anticlinal. A. M. Kuznetsov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 159—163).—Well waters in Kama basin contain up to 1 g. of H_2S per l. The $[\text{H}_2\text{S}]$ usually is the higher the longer the H_2O was underground. H_2S probably is produced by bacteria from CaSO_4 and petroleum. Analyses are given. J. J. B.

Diurnal fluctuation of oxygen and pH in fresh waters. R. J. Whitney (*J. Exp. Biol.*, 1942, 19, 92—99). G. P. W.

Thiamin in lake waters and aquatic organisms.—See A., 1944, III, 199.

Calcareo-dolomitic muds of the Balkhash lake. D. G. Saposhnikov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 150—153).—The greatest proportion of the dolomite occurs in the eastern part of the lake, the examination being carried out colorimetrically with an alkaline solution of diphenylcarbazine (Feigl reaction). Samples rich in dolomite were also thermoanalysed. The dolomite content of the western part is probably small. There is a decrease of 34.1% dolomite for an increase in depth of 60 cm. for the bottom deposits. There is also an appreciable dolomite content in the mud of the south-west of the lake. The conditions of formation of these muds are unknown. J. O'M.-B.

Alleged mineral zoning at Mt. Isa. R. Blanchard (*Amer. Inst. Min. Met. Eng.*, 1943, *Tech. Publ.* 1652, 27 pp., *Min. Tech.*, 7, No. 6).—The mineral sulphide succession at Mt. Isa is described. The unorthodox mineral succession and pattern of mineral distribution is shown to be the natural outcome of conditions that prevailed during the period of ore deposition. Doubt is thrown on the premises on which the zonal theory of mineral succession is based. L. S. T.

Talc deposits at D'Urville island and Cape Horn, Admiralty Bay. E. O. Macpherson (*New Zealand J. Sci. Tech.*, 1943, 24, B, 219—227).—Deposits at Rock Point and Cherry Bay, and near Cape Horn, are described, and their geology is outlined. L. S. T.

Talc in north-west Nelson and north Westland. H. W. Wellman (*New Zealand J. Sci. Tech.*, 1943, 24, B, 227—235).—Ten deposits or groups of deposits are described. L. S. T.

Formation of concretions. T. I. Chandamirov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 209—211).—The formation of concretions by the ferrugination of clayey boulders is discussed. The boulders of clay are penetrated and enriched to varying extents by ferrous salts from circulating waters. Evidence of this view is provided by the ferrugination of clay boulders in the Kirmakinski valley. L. S. T.

Apatites of two textural types from apatite-nepheline rocks of Chibiny. A. I. Volodtschenkova and B. N. Melentev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 34—35).—Analyses of two apatites—mottled and breccia-like—from the tundra of Chibiny are given. A. J. M.

(A) Cordierite crystals from a glass furnace. (B) Cordierite from Horns Nek, Transvaal. S. J. Shand (*Amer. Min.*, 1943, 28, 391—395).—(A) The formation of cordierite (I) on the walls of a glass tank in which the fused mass consisted of Al silicate and Mg borosilicate glass is described. The (I), ρ 2.516, n 1.5223 \pm 0.0003, γ 1.5270 \pm 0.0003, contained SiO_2 50.77, Al_2O_3 35.26, CaO 1.24, MgO 12.72, H_2O 0.25, total 100.24%.

(B) In the nepheline granophyre from Horns Nek the mineral is cordierite and not nepheline. L. S. T.

Crystal structure of gillespite, $\text{BaFeSi}_4\text{O}_{10}$. A. Pabst (*Amer. Min.*, 1943, 28, 372—390).—Rotation, oscillation, Laue, and powder X-ray patterns show that $a_0 = 7.495 \pm 0.010$ and $c_0 = 16.050 \pm 0.010$ Å., the space-group is $D_{2h}^{16} - P4/ncc$, and the unit cell contains 4 $\text{BaFeSi}_4\text{O}_{10}$. $\rho_{\text{calc.}}$ is 3.407 and $\rho_{\text{obs.}}$ 3.40 \pm 0.02. A structure with 11 parameters gives agreement between calc. and observed intensities; it is a silicate sheet-structure with O atoms in 3 kinds of positions and unshared corners of SiO_4 tetrahedra on both sides of the sheets. Single and double Fourier summations check the structure. Ba has an 8-fold and Fe a 4-fold co-ordination. The changes produced by leaching in apophyllite, gillespite, and biotite with removal of cations and addition of H_2O are similar. The flakes retain their shape and some of their optical properties, but yield no X-ray powder diffraction pattern. L. S. T.

Crystallography of acanthite, Ag_2S . L. S. Ramsdell (*Amer. Min.*, 1943, 28, 401—425).—Weissenberg and powder photographs give a_0 9.47, b_0 6.92, c_0 8.28, vol. of unit cell 449.8 Å.³, and 8 Ag_2S . $\rho_{\text{calc.}}$ is 7.27 and the probable space-group is $B2_1/c$ (C_{2h}). The observed cell dimensions and the twinning are such that the monoclinic symmetry is easily reconciled with the previous assignment of acanthite to the orthorhombic and to the cubic systems. L. S. T.

Alkaline vitrophyre dyke, Cape Neddick, Maine. J. C. Haff (*Amer. Min.*, 1943, 28, 426—436).—A petrographic description of an unusual alkaline vitrophyre dyke intruding a mass of breccia is given. Chemical analysis [F. A. Gonyer] indicates its strong nordmarkitic or solvsbergitic affinities. L. S. T.

Genesis of granitic pegmatites. N. M. Uspensky (*Amer. Min.*, 1943, 28, 437—447).—The pegmatite veins of Gold Mountain with accompanying graphic granite originated by a pneumatolytic-hydrothermal transformation of aplite dykes. The active agents in this process were aq. siliceous alkaline solutions containing a small amount of F[−]. L. S. T.

Bixbyite-sitaparite-partridgeite. (A) J. E. de Villiers. (B) M. Fleischer (*Amer. Min.*, 1943, 28, 468—469, 469).—(A) Partridgeite should be applied to Mn-Fe-sesquioxides containing <10% Fe_2O_3 , sitaparite to those containing 10—30% Fe_2O_3 , and bixbyite to the mineral containing >30% Fe_2O_3 .

(B) The name sitaparite should be discarded. L. S. T.

Autoradiography of minerals. C. Goodman and G. A. Thompson (*Amer. Min.*, 1943, 28, 456—467).—Autoradiographic studies of some common minerals have been made, the stray slow neutrons from a cyclotron being used (cf. A., 1943, I, 241). The distribution of Mn, Au, Cu, W, P, K, Ba, Na, and As revealed by the autoradiographs (reproduced) of these minerals is discussed. L. S. T.

Parkerite, $\text{Ni}_3\text{Bi}_2\text{S}_8$, from Sudbury, Ontario. Re-definition of the species. C. E. Michener and M. A. Peacock (*Amer. Min.*, 1943, 28, 343—355).—Parkerite (I), orthorhombic, $\rho_{\text{obs.}}$ 8.4, $\rho_{\text{calc.}}$ 8.50, a_0 4.02, b_0 5.52, c_0 5.72 Å.; probable space-group $Pmm2 - C_{2v}^2$, contains one $\text{Ni}_3\text{Bi}_2\text{S}_8$ per unit cell. A chemical analysis [W. Wagner] and X-ray data are given. (I), hardness 3 (B+), is non-magnetic, and a good electrical conductor. It is sol. in conc. HNO_3 , but not in conc. HCl . A spectrographic analysis showed the presence of Ni, Bi, and traces of Cu and Sn, and the absence of Fe, Mn, W, Ti, Sc, Co, Pd, Ag, Cd, Ir, Pt, Te, As, and Sb. (I) occurs sparingly embedded with galena, sulphides, arsenides, and tellurides, in the extremities of one of the ore-bodies in the Sudbury district. It can be synthesised in cryst. masses by fusing the elements in N_2 or in a vac. L. S. T.

Mineralogy and genesis of hydroxylapatite. L. Mitchell, G. T. Faust, S. B. Hendricks, and D. S. Reynolds (*Amer. Min.*, 1943, 28, 356—371).—X-Ray powder photographs of Swiss hydroxylapatite (I) and of a new occurrence of (I) from Cherokee Co., Georgia, are reproduced; the patterns are similar to those obtained from fluorapatite (II) and synthetic (I). Optical properties, recorded for these and other apatites, show that the presence of OH for F increases the vals. of n . ρ for (I) and (II) are practically identical. The Swiss (I) is actually a fluor-(I). Chemical analyses are recorded and discussed. Spectroscopic determination of Cu in 4 synthetic samples of (I) showed a correlation between intensity of pink colour and the presence of adventitious Cu. The pink colour is easily seen in a sample containing 0.003% Cu. Petrology is described and genesis discussed. (I) is found associated only with talc and chlorite schists; this indicates that it is formed by metamorphism in presence of much H_2O , and with simultaneous formation of other minerals rich in OH group. L. S. T.

Electrochemical properties of clay minerals. Differentiation of hydrogen clays and bentonites by electrochemical methods.—See A., 1944, I, 60.

Thermal analysis of clay minerals and acid extraction of alumina from clays.—See B., 1944, I, 133.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A I—General, Physical, and Inorganic Chemistry.

MAY, 1944.

I.—SUB-ATOMICS.

Polarisation of lines in the night-sky luminescence spectrum. V. L. Ginzburg (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 237—240).—A discussion of the degree of polarisation in the lines λ 5577 and 6300 Å. of O and the D lines of Na, assuming that the luminescence is due to fluorescence and multiple scattering of the sun's rays. The possibility of polarisation in the aurora spectrum is also discussed. H. J. W.

Spectrum of doubly ionised cadmium. K. C. Mazumder (*Indian J. Physics*, 1943, 17, 229—238).—The spark spectrum of Cd has been investigated from 2200 to 370 Å. and the lines corresponding with different stages of ionisation have been sorted out. 134 new lines of Cd III have been classified, identifying 29 new terms with $4d^9 6s$, $4d^9 5d$ configurations, and 7 undesignated terms. Term vals. have been calc. The deepest term, $4d^{10} 1S_0$, is 308,463 cm.⁻¹ and the ionisation potential ~33 v. W. R. A.

Observation of very small Stark effects. L. Jenckel and H. Kopfermann (*Z. Physik*, 1941, 117, 145—155).—A beam of atoms is illuminated at right angles from a source emitting the resonance frequency for which the inverse Stark effect is to be examined, and an electric field of $>300,000$ v. per cm. is applied at right angles to the light and atom beams. The absorption in the "continuum" provided by the emitted line is observed by means of a Fabry-Perot étalon. The Ca 1S_0 — 1P_1 (λ 4227 Å.) line first shows measurable red displacement at ~200 kv. per cm. Higher potential gradients are required than those predicted by theory, e.g., 300 kv. per cm. produces $\Delta\nu = 1.8 \times 10^{-2}$ cm.⁻¹ L. J. J.

Probable X-ray mass absorption coefficients for wave-lengths shorter than the K critical absorption wave-length. J. A. Victoreen (*J. Appl. Physics*, 1943, 14, 95—102).—Graphic analysis of all available experimental data leads to an expression for absorption coeffs. $\mu/\rho = a\lambda^3 Z - (2Z/A) - \beta\lambda^4 Z^5 (2Z/A) + \alpha_e N_0 (Z/A)$, valid for all elements, where $a = aZ - bZ - c$ and $dZ^2 - eZ + f$. Different vals. of a , b , c , d , e , and f are required for each side of the crit. absorption $\lambda\lambda$ and for either side of $Z - 5$, and are given for the short- λ side of the K crit. absorption $\lambda\lambda$. Vals. of $aZ^2 (2Z/A)$ and $\beta Z^5 (2Z/A)$, calc. for all elements, are tabulated. Calc. mass absorption coeffs. agree well with published data as shown by comparative tabulations for a representative range of elements and $\lambda\lambda$. N. M. B.

L Spectra and characteristic levels of thallium. (Mlle.) Y. Cauchois (*Compt. rend.*, 1942, 215, 413).—Vals. of λ and ν/R are reported for transitions, in emission and absorption, from the L_I , L_{II} , and L_{III} levels. ν/R vals. for levels from K to O_V (except N_{VI} , VI , and O_I) are derived. A. J. E. W.

L Spectra and characteristic levels of gold. (Mlle.) Y. Cauchois (*Compt. rend.*, 1942, 215, 465—466).—Corresponding data are reported for Au (cf. preceding abstract). A. J. E. W.

"Avalanche products," discharge depressions, and falling characteristics. W. Rogowski (*Z. Physik*, 1941, 117, 265—284).—The effect of irradiation on electrical discharge characteristics in H_2 , N_2 , air, A, Ne, Kr, and Xe is discussed. L. J. J.

Thermionic emission from an oxide-coated cathode. H. Y. Fan (*J. Appl. Physics*, 1943, 14, 552—560).—Electrons emitted from an indirectly heated BaO-coated cathode have a Maxwellian distribution corresponding with the temp. of the cathode in the range 682—951° K. With accelerating voltages up to 2500 v. per cm., the current increases much more rapidly than is predicted by Schottky's theory. Both the work function and factor A vary with the physical state of the cathode. No decay of emission with time is found. L. J. J.

Secondary electron emission from metals in the low primary energy region. (Miss) I. Gimpel and (Sir) O. Richardson (*Proc. Roy. Soc.*, 1943, A, 182, 17—47).—A new method and apparatus for measuring secondary electron emission from non-gaseous material are described. One of the essential features of the experimental arrangement is the control of the primary beam of electrons by an electrostatic lens system. The method is applied to pure, gas-free Cu, using primary electrons with energies as low as 0.35 v. It is concluded that for low-energy electrons the secondary electrons are just re-

flected electrons and that the coeff. of reflexion is independent of the energy. No manipulation of the electrode potentials can reduce the mean energy of electrons from a thermionic source at temp. T below $2kT$. G. D. P.

Electron affinity of oxygen. D. T. Vier and J. E. Mayer (*J. Chem. Physics*, 1944, 12, 28—34).—Measurements of the ratio of negative ions to electrons leaving a hot filament surface exposed to O_2 at 0.1—2 μ . and 2030—2230° K. give 70.8 ± 2.0 kg.-cal. per g.-mol. for the reaction $e^- + O_{gas} \rightarrow O_{gas}^-$ at 0° K. L. J. J.

Condensation nuclei made visible by the electron microscope. F. Linke (*Naturwiss.*, 1943, 31, 230—231).—A magnification of 30,000, obtained with the electron microscope, makes visible the nuclei (radius 25—100 m μ .) responsible for condensation of H_2O vapour. Photographs are given, and the structure of the nuclei is discussed. A. J. M.

Control of rare-gas-filled low-pressure arcs by means of a grid in the discharge plasma. E. Leimberger (*Z. Physik*, 1941, 117, 621—641).—The anode current can be controlled by means of a positive space charge layer produced by a grid. At relatively high pressures control is limited by constriction of the arc. The dependence of the control effect on a no. of variables has been studied. L. J. J.

Electric spark discharge in different gases. T. E. Allibone and J. M. Meek (*J. Sci. Instr.*, 1944, 21, 21—27).—A survey, with illustrative data and curves, of breakdown of the nearly uniform and the diverging field for const. and low-frequency alternating voltage and for impulse voltage. N. M. B.

Mechanism of electrical removal of gas at pressures below 10^{-4} torr. H. Schwarz (*Z. Physik*, 1941, 117, 23—40).—Sudden changes in electron current between 0.1 and 30 ma., observed in high-vac. hot-cathode tubes with annular anodes, at 4000 v. anode potential, are caused by reversal of the charge on the glass wall. The charge is independent of pressure between 2×10^{-7} and 2×10^{-3} torr., and is determined by the secondary electron emission yield (δ) of the wall. The charge on the wall is positive for $\delta > 1$ and negative for $\delta < 1$. The electrical conditions can be reproduced by the introduction of a metal wall, the potential of which can be varied. The change in the anode current from a higher to a lower val. is accompanied by a sudden fall in pressure from 10^{-4} to 10^{-6} torr., caused by capture of positive ions by the wall. When a wide-meshed wire network is used, absorption of gas is found only in the range +30 to +140 v. L. J. J.

At. wt. of samarium. O. Honigschmid and F. Hirschbold-Wittner (*Z. physikal. Chem.*, 1941, A, 189, 38—43).—Pure Sm_2O_3 was prepared, and converted into $SmCl_3$ by pptg. as oxalate, igniting, and dissolving in HCl. The pure $SmCl_3$ was titrated against Ag by the nephelometric method, and compared with Ag by weighing the pptd. AgCl. The average val. of the at. wt. was 150.38. A. J. M.

Scattering of rapid neutrons at protons and deuterons. M. Ageno, E. Amaldi, D. Bocciarelli, and G. C. Trabacchi (*Naturwiss.*, 1943, 31, 231—232).—With an arrangement of three proportional counters in coincidence the total cross-sections of neutrons of 4.1, 12.5, and 13.5 Me.v. are measured with respect to C, H, and D. The results agree with Bethe's theory. A. J. M.

and γ -Rays from artificially radioactive ^{74}As . K. Philipp and F. Rehbein (*Naturwiss.*, 1943, 31, 235—236).—The β -spectrum of ^{74}As has been investigated with a magnetic β spectrograph. There are 3 components with limiting energies 1.1 ± 0.1 , 2.7 ± 0.2 , and 3.15 ± 0.05 Me.v. Weak electron lines were also found in the region of 0.3—0.7 Me.v. The energies of γ -radiations obtained from these data agree with experimental results. A. J. M.

Continuous β -ray spectrum emitted by radiovanadium, ^{55}V . (Mlle.) T. Yuasa (*Compt. rend.*, 1942, 215, 414—416).—The β -ray spectrum of radio-V prepared by neutron bombardment of V_2O_5 in a cyclotron has been examined by the Wilson cloud-chamber method. The spectrum is simple; with a source containing 24 mg. of V_2O_5 per sq. cm. the upper energy limit is 2.65 ± 0.05 Me.v.; the most probable and mean energies, respectively, are 0.90 ± 0.05 and 1.1 Me.v. γ -Radiation of mean energy 1.57 ± 0.10 Me.v. and a small no. of positrons of energy 0.15—0.97 Me.v. are observed.

The β - and γ -radiations are ascribed to the reactions $^{52}_{24}\text{Cr} \rightarrow ^{52}_{24}\text{Cr}^* \rightarrow ^{52}_{24}\text{Cr}$.
A. J. E. W.

Active strontium and yttrium isotopes obtained in uranium fission. O. Hahn and F. Strassmann (*Naturwiss.*, 1943, 31, 249–250).—Preliminary. Two new isotopes, Sr with half-life ~ 2 min., and its daughter element Y of half-life 20 min., have been detected in the product from active U. The half-life of the Y isotope from 7-min. Sr is 11.5 ± 0.5 hr. instead of the earlier val. 9 hr. The half-life of the Sr isotope, found by Gotte (*ibid.*, 1941, 29, 496), is 10 hr. instead of the earlier val. 8.5 hr.
J. F. H.

Theory of mesons. K. Nikolski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 173–175).—Mathematical.
N. M. B.

Production of cosmic-ray mesons. L. Jánosy (*Physical Rev.*, 1943, [ii], 64, 345–349).—The cross-sections given (cf. Hamilton, *et al.*, A., 1944, I, 2) for the production of mesons in collisions between heavy particles are so large that a heavy particle crossing an atom nucleus must be expected to collide several times inside the same nucleus. This accounts for cloud-chamber observations showing the production of several mesons in one point. Anticoincidence experiments can be interpreted by the theory (*ibid.*), when the occurrence of multiple collisions is assumed.
N. M. B.

Mesotron temperature coefficient. F. A. Benedetto (*Physical Rev.*, 1943, [ii], 64, 317–318; cf. A., 1942, I, 37).—Causes of the discrepancy between observations by counter train and by ionisation chamber are discussed.
N. M. B.

Applications of the λ -limiting process to the theory of the meson field. W. Pauli (*Physical Rev.*, 1943, [ii], 64, 332–344).—Mathematical. The Wentzel-Dirac λ -limiting process for the interaction of an electron with an electromagnetic field is applied to the interaction of a heavy particle (nucleon) with the meson field.
N. M. B.

Stellar model built in complete accordance with Bethe's formula of energy-generation. N. R. Sen and U. R. Burman (*Physical Rev.*, 1943, [ii], 64, 317).—Bethe's scheme for stars produced by the "C cycle" requires a temp. of $\sim 20 \times 10^6$ degrees. A preliminary investigation to find what types of core with that central temp., H_2 content 36%, He content 0, and average mol. wt. 1, conform to Bethe's formula is reported. Distinguishing a convective and an energy core, for central density $\rho < 31$ g. per sq. cm. there is no convective core, for ρ 31–51 g. per sq. cm. there is a convective core, and for $\rho \geq 51$ g. per sq. cm. the model is entirely convective. Other characteristics are evaluated and discussed.
N. M. B.

II.—MOLECULAR STRUCTURE.

Molecules in stellar atmospheres. P. P. Dobronravov (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 91–94).—The temp. of stars and the conditions of some mols. at their surfaces are deduced from the mol. bands in stellar spectra.
J. J. B.

Resonance emission of cadmium hydride bands in cadmium-photo-sensitised reactions of hydrocarbons. E. W. R. Steacie and D. J. LeRoy (*J. Chem. Physics*, 1944, 12, 34–36).—The resonance excitation of CdH bands in mixtures of C_2H_4 or C_2H_2 with Cd vapour illuminated with $\lambda\lambda$ 3261 and 2288 Å. has been examined. With λ 2288 Å. no resonance emission was found. With λ 3261 Å., no resonance excitation was found with C_2H_4 , but CdH bands were emitted with C_2H_2 . Thus the primary process in Cd-sensitised reactions of paraffins is $\text{Cd}(^6\text{P}_1) + \text{RH} \rightarrow \text{CdH} + \text{R}$.
L. J. J.

Band spectrum of N_2 ; weak systems in the visible region. A. G. Gaydon (*Proc. Physical Soc.*, 1944, 56, 85–95).—Data are reported for the Goldstein-Kaplan bands at $\lambda\lambda$ 4165, 4432, and 4728, which appear readily in the spectrum produced by mild excitation with a silent, ozoniser-type discharge, and with a Tesla coil. Measurements support Kaplan's vibrational analysis, but other bands in the ultra-violet probably belong to a different system. The rotational structure and probable type of electronic transition are discussed. A weak new system observed in the green has, provisionally, $\omega_1' = 896$, $\omega_1'' = 740$ cm^{-1} . The electronic levels of N_2 , effect of excitation conditions on the band systems, and the bearing of results on the determination of dissociation energy are discussed.
N. M. B.

Band spectrum of NO: γ and ϵ systems. A. G. Gaydon (*Proc. Physical Soc.*, 1944, 56, 95–103).—Data are reported for the γ , δ , and ϵ bands of NO excited by transformer discharge and silent ozoniser-type discharge. Measurements and intensity distribution show that, contrary to the findings of Herzberg (cf. A., 1940, I, 191), the γ and ϵ systems arise from separate upper electronic states. There is no evidence of predissociation in the γ and ϵ systems. It is difficult to reconcile observations with a heat of dissociation as low as 5.29 e.v.
N. M. B.

Spectroscopic study of the diffuse discharge in nitrogen at atmospheric pressure. J. Janin (*Compt. rend.*, 1942, 215, 505–506).—The ultra-violet spectrum includes bands of the second positive system of N_2 , a few of the negative bands of N_2^+ , and the Vegard-

Kaplan ($A \rightarrow X$) bands of N_2 . The forbidden $^4\text{S} \rightarrow ^3\text{P}$ line of N also appears at 3466.5 ± 0.1 Å., its intensity variation being parallel to that of the $A \rightarrow X$ bands. $\lambda\lambda$ of eight of the band-heads of the $A \rightarrow X$ system are recorded, and a ν formula is proposed; all the bands have P and R branches. Details of fine structure are given for the (1, 8) and (1, 9) bands (2997, 3198 Å.).
A. J. E. W.

Green phosphorescence of active nitrogen. (Mme.) R. Herman (*Compt. rend.*, 1942, 215, 506–508).—The phosphorescence is produced by a high-voltage discharge in purified N_2 at 10–20 mm. pressure. The spectrum contains high vibrational lines of the first positive system of N_2 at high intensity; in addition to the levels $\nu' = 13$ –20 of the sequence $\nu' - \nu'' = 5$, the sequence $\nu' - \nu'' = 6$ ($\nu' = 17$ –24) is observed. Although first positive N and first negative N_2^+ bands occur simultaneously in the spectrum, a comparison of intensities shows little similarity to auroral spectra.
A. J. E. W.

New ultra-violet band-system of antimony monoxide (SbO). A. K. Sengupta (*Indian J. Physics*, 1943, 17, 216–222).—A new ultra-violet band system, probably a $^2\Sigma \rightarrow ^2\Pi$ transition, has been photographed in the region 2910–2450 Å. in the emission spectrum of SbO . The bands are double-headed and degraded towards the violet. The vibrational structure analysis shows that the lower state of the new system is identical with that of other SbO systems already known.
W. R. A.

Ultra-violet spectra and electron configuration of HgF and related halide molecules. H. G. Howell (*Proc. Roy. Soc.*, 1943, A, 182, 95–112).—The high-frequency ultra-violet emission spectrum of HgF was photographed and analysed into two systems, each due to a $^2\Pi \rightarrow ^2\Sigma$ transition between Hg atom-like levels. Predicted analogies with the Zn and Cd halides are verified. The electron configuration of the states involved is discussed and an energy-level diagram is given.
G. D. P.

Assay of potassium *p*-phenolsulphonate, its pH range, and its ultra-violet absorption spectrum. E. E. Sager, M. R. Schooley, and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1943, 31, 197–204; cf. also C., 1944, Part 2).—The purification of $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{K}$ (I) and its determination through the quantity of Br used in its dibromination are described. The absorption spectrum of (I) has been determined over the λ range 2100–3100 Å. The main absorption band has a peak at 2300 Å. but this is sharply defined only in dil. solutions. The absorption spectrum is changed considerably on the addition of NaOH, owing to the production of the bivalent ion.
J. W. S.

Ultra-violet absorption spectra and resonance in benzene derivatives: sulphanilamide, metanilamide, *p*-aminobenzoic acid, benzenesulphonamide, benzoic acid, and aniline. W. D. Kumler and L. A. Strait (*J. Amer. Chem. Soc.*, 1943, 65, 2349–2354).—Ultra-violet absorption spectra of sulphanilamide (I), metanilamide (II), $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (III), $\text{PhSO}_2\cdot\text{NH}_2$ (IV), BzOH (V), and $\text{NH}_2\cdot\text{Ph}$ (VI) have been determined in acidic, basic, H_2O , and aq. NaCl solutions. The spectra are correlated with the known resonance forms. Spectra of (I) and (II) in acid are similar to that of (IV) in H_2O . The spectrum of an unsubstituted or alkyl-substituted aromatic NH_2 -compound reverts, in a solution sufficiently acid to cause conversion into the salt, to that of the compound in which NH_2 is replaced by H or an alkyl group. (I) and (III) have higher extinction coeffs. in basic solution than in H_2O or aq. NaCl, indicating a greater contribution by the main resonance form to the ion than to the undissociated mol. The reverse is true for (IV) and (V). Solvent effects in the spectra of compounds of the type of $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (VII) are due to solvation differences and not to differences in dielectric const. Differences in the spectra of (VII) in C_6H_{14} , dioxan, and H_2O are attributed to differences in H-bonding. The similarity of the spectra of (VI) and (II) is attributed to the incompatibility of NH_2 and $\text{SO}_2\cdot\text{NH}_2$ resonance in (II), that due to NH_2 effectively concealing the resonance of $\text{SO}_2\cdot\text{NH}_2$.
W. R. A.

Ultra-violet absorption spectra of ethanol lignins.—See A., 1944, II, 115.

γ Bands in absorption spectra. G. N. Lewis and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1943, 65, 2102–2106).—When one of the equiv. groups of crystal-violet is replaced by a different group, the single absorption band becomes resolved into α and γ bands. The larger is the difference in auxochromic nature of the new and old groups, the wider is the separation of the α and γ bands. The second band in malachite-green is proved to be a γ band by production of oriented mols. in a rigid solvent and by polarised fluorescence. It is shown that the electronic oscillations of two excited states are perpendicular to each other. The negative fluorescent polarisations in fluorescein and rhodamine-B accord with Lewis and Calvin's theory. A new method of measuring small degrees of polarisation is described. (See also C., 1944, Part 2.)
W. R. A.

Second order α -bands in absorption spectra. G. N. Lewis and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1943, 65, 2107–2110).—Additional second-order α bands in the absorption spectra of cyanines and other dyes are reported and discussed.
W. R. A.

Ultra-violet absorption spectra of alicyclic di- and tri-ketones.—See A., 1944, II, 138.

Absorption spectra and structure of pyrethrins I and II. A. E. Gillam and T. F. West (*J.C.S.*, 1944, 49—51; cf. A., 1942, I, 31).—The presence in pyrethrolone enol semicarbazone (I) of conjugated, and not cumulated, ethylenic linkings in the side-chain is proved by absorption max. at 2260—2270 and 3085—3090 Å. in EtOH. (I) has m.p. 255—256°, but ϵ varies for different samples (12,000—17,600 and 16,500—20,300 for the two bands, respectively). For the enol itself (II) (modified prep.) the two bands overlap, giving a max. at 2440 Å. (ϵ 12,600). Pyrethrolone (III) has a max. at 2260 Å. (ϵ ~29,000). (II), (III), and the Me ether of (III) are either unchanged or converted into high-boiling compounds by $\text{Al}(\text{OPr}^i)_3$ - Pr^iOH . R. S. C.

Volatile vegetable matter. XXVIII. Ultra-violet absorption and Raman spectra of ionones and related substances. Y. R. Naves and P. Bachmann (*Helv. Chim. Acta*, 1944, 27, 97—104).—For a solution of the ionones (I) in hexane there is a series of fine bands in the ultra-violet which are connected with the states of vibration of the normal mol. In α -ionone and methyl- α -ionone the R absorption bands are continuous with the K bands. The frequencies characteristic of different double-bond effects and the displacements which cause coupling can be determined by comparison of the Raman spectra of (I) with those of the dihydroionols. Secondary effects in the spectra are mostly explicable by conjugation. J. O'M. B.

Fluorescence and absorption spectra of naphthalene and its derivatives at low temperatures. A. F. Prichotko and K. G. Schabaldas (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 120—125).—The absorption and fluorescence spectra of C_{10}H_8 and the fluorescence spectra of 2- $\text{C}_{10}\text{H}_7\text{Me}$, 2:6- $\text{C}_{10}\text{H}_6\text{Me}_2$, α - and β - $\text{C}_{10}\text{H}_7\text{OH}$, α - and β - $\text{C}_{10}\text{H}_7\text{NH}_2$, and dinaphthyl are determined at 20.4° K. Several new electron transitions are reported. J. J. B.

Fluorescence of anthracene in the presence of naphthalene. S. C. Ganguly (*Proc. Indian Assoc. Cult. Sci.*, 1943, 26, 7).—Fluorescence of naphthalene (I) has been studied in solid solution with anthracene (II) and chrysene, also in EtOH and in an EtOH solution of (II). In solid solution the excited fluorescence bands of (I) are shifted slightly, depending on the solvent. Comparison of the fluorescence of mixed EtOH solutions of (I) and (II) with solutions containing only (I) or (II) shows that the fluorescence of one component is not affected by the presence of the other. Absorption spectra of the solutions confirm this result. W. R. A.

Raman spectra of solutions of silver perchlorate in toluene and in water. M. J. Murray and F. F. Cleveland (*J. Amer. Chem. Soc.*, 1943, 65, 2110—2112).—A band at 167 cm^{-1} in the Raman spectrum of a conc. solution of AgClO_4 in PhMe, which has no counterpart in aq. AgClO_4 , but appears in aq. $\text{Hg}(\text{ClO}_4)_2$, is thought to arise from a covalent linking of the metal and ClO_4 . W. R. A.

Raman effect. CXXVIII. Oxalic acid. L. Kahovec, K. W. F. Kohlrusch, and J. Wagner. **CXXIX. Nitrogen compounds. XIX. Amides of dicarboxylic acids and related compounds.** L. Kahovec and J. Wagner. **CXXX. Nitrogen compounds. XX. Tetranitromethane.** K. W. F. Kohlrusch and H. Wittek (*Z. physikal. Chem.*, 1941, B, 49, 145—155, 156—162, 163—169).—CXXVIII. The Raman spectra of anhyd. cryst. α - and β - $\text{H}_2\text{C}_2\text{O}_4$ are obtained. They differ markedly between themselves and also differ from that of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. β - $\text{H}_2\text{C}_2\text{O}_4$ gives four lines at 2600—3100 Å., and the α -form two at 3100 and 3260 Å., ascribed to O—H—O bridges. No satisfactory explanation of the observed vibrational spectra can be obtained by discussion of the results of X-ray, Raman, and infra-red spectra.

CXXIX. The Raman spectra of cryst. $(\text{CO} \cdot \text{NH}_2)_2$ (I), $\text{CH}_3 \cdot \text{CO} \cdot \text{NH}_2$, $(\text{CH}_3 \cdot \text{CO} \cdot \text{NH}_2)_2$, $\text{NH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$ (II), $\text{NH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{Me}$, $\text{NH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, $(\text{CH}_3 \cdot \text{CO})_2\text{O}$, $(\text{CH}_3 \cdot \text{CO})_2\text{NH}$, allantoin, and $(\text{CO} \cdot \text{NH})_2\text{CO}$ are obtained. The $\delta(\text{NH}_2)$ and $\nu(\text{NH}_2)$ frequencies and the similarity of the spectra of (I) and (II) to those of $\text{H}_2\text{C}_2\text{O}_4$ and N_2O_4 are briefly discussed.

CXXX. The Raman spectra of $\text{C}(\text{NO}_2)_4$ as solid, liquid, and dissolved in CCl_4 are obtained. The results confirm those of Medard (A., 1935, 564). The results of polarisation measurements are best explained by a structure with symmetry S_{4w} . J. F. H.

Rectifying property of carborundum. J. T. Kendall (*Proc. Physical Soc.*, 1944, 56, 123—129).—A technique is described for obtaining non-rectifying C-carborundum contacts. Current-voltage curves for single rectifying contacts show that (I) green, and (II) blue or black carborundum are essentially different types of semi-conductor; in (I) rectification takes place so that easy electron flow is from semi-conductor to metal, and in (II) rectification is in the opposite direction. Experiments show that all rectification takes place at the contact surface and that vol. rectification (if any) is a second-order effect. N. M. B.

Dielectric constant of ionised air in a discharge tube in the range of wave-lengths 80—1500 cm. N. Alam and S. R. Khastgir (*Indian J. Physics*, 1943, 17, 204—215).—The effective dielectric const., ϵ , of the ionised air in a discharge tube has been determined, using

the Lecher-wire method, for λ 80—1500 cm. Three distinct min. were observed at 175, 310, and 370 cm., corresponding with weak oscillations, of λ 169, 310, and 362 cm., produced within the tube under the conditions of measurement. W. R. A.

Hydrogen cyanide. XIII. Dielectric constant of anhydrous hydrogen cyanide. G. E. Coates and J. E. Coates (*J.C.S.*, 1944, 77—81).—The dielectric const. (ϵ) of anhyd. HCN can be represented by $\log \epsilon = 2.199 - 0.0079\theta + 5 \times 10^{-5}\theta^2$ for θ 13.3° (f.p.) to 18°, and by $\log \epsilon = 2.1899 - 0.00633\theta$ for θ 18—25.7° (b.p.). The high vals. of ϵ and temp. coeff. are interpreted in terms of linear polymerisation and the existence of mol. units with large dipole moments. C. R. H.

Scattering of light by small drops of water. R. Ruedy (*Canad. J. Res.*, 1943, 21, A, 99—109).—When small drops increase in size to $2r = 0.25\lambda$, they scatter light according to Rayleigh's law, but for $2r = 0.25 - 0.5\lambda$ the intensity of light scattered towards the source decreases almost to zero, the change being most marked for $2r = 0.25 - 0.375\lambda$. The sharp increase, $\propto r^6$, of scattered light with increase in size continues in the main direction of radiation by the particle. As scattering deviates from Rayleigh's law, colours other than blue appear strongly; the dispersion of the colours increases with increasing particle size until mainly red light remains. N. M. B.

Rotation dispersion of some α -hydroxy-acids. Configuration of α -hydroxy-acids. P. Szarvas (*Z. physikal. Chem.*, 1941, A, 188, 235—245).—The rotatory dispersions of (+)-lactic (I), (—)- α -hydroxybutyric (II), (—)-malic, and (+)-tartaric acids in the visible and near ultra-violet regions have been determined. The results indicate that (II) has the l -configuration similar to (I). The contrary observation of Levene and Haller (A., 1927, 1053) is attributable to the presence of BaCl_2 . J. W. S.

Possibility of determining experimentally the coefficient of damping of elastic waves of the Debye spectrum from observations on the fine structure of lines of Rayleigh scattering. V. V. Vladimirski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 201—202).—Determination of coeff. of damping may be possible from investigation of the fine structure in a non-uniformly heated body. F. R. G.

Interferometric studies of light scattering in binary liquid mixtures. I. K. S. Bai (*Proc. Indian Acad. Sci.*, 1943, 18, A, 210—217).—The light scattered by H_2O and a series of org. liquids when illuminated with the λ 4810 Å. line of Zn is found to have Brillouin components. These are present also in the scattered light from ordinary mixtures, e.g., $\text{EtOH}-\text{H}_2\text{O}$ and $\text{C}_6\text{H}_6-n\text{-C}_6\text{H}_{14}$, but are absent in that from the crit.-composition mixtures of MeOH and $n\text{-C}_6\text{H}_{14}$ and of $\text{Pr}^i\text{CO}_2\text{H}$ (I) and H_2O at the crit. solution temp. (~20°), and at temp. up to 40° for $\text{MeOH}-n\text{-C}_6\text{H}_{14}$. For (I)- H_2O the components appear weakly at 90°. It is concluded that the mixtures remain as emulsoids over a range of temp. above 20°, the mol. aggregates being of a size comparable with λ . H. J. W.

Diffuse reflexion of light by a foggy medium. V. A. Ambarzumian (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 229—232).—The scattering power of a medium of infinite thickness with a plane boundary is unaltered by the addition of a further thin layer. Hence an integral equation, the solution of which determines the scattered intensity in any direction outside the boundary, is deduced. The method is also applicable to a finite slab. Solutions of the equations are not given. H. J. W.

Distribution of light intensity within a scattering medium. R. R. Newton (*J. Appl. Physics*, 1943, 14, 481—486).—An integral-differential equation is derived for intensity as a function of position and direction. L. J. J.

Doppler effect in a refractive medium. I. M. Frank (*J. Physics U.S.S.R.*, 1943, 7, 49—67).—Theoretical. A. J. M.

Valency states of sulphur. E. N. Gurjanova (*J. Phys. Chem. Russ.*, 1943, 17, 65—74).—The energies of various possible structures of SO_2 , SO_3 , SOCl_2 , and SO_2Cl_2 are calc. The most probable structures are $\text{O}:\text{S}:\text{O} \rightleftharpoons \text{O}^-\text{S}^+\text{O}$, $\text{Cl}_2\text{S}:\text{O} \rightleftharpoons \text{Cl}:\text{S}(\text{Cl})\text{O}$, $\text{O}:\text{S}^+(\text{O})_2$, and $\text{Cl}_2\text{S}(\text{O})_2$. Other chemical evidence confirms the presence of a tervalent S ion in "quadrivalent," and of a quadrivalent S ion in "sextavalent" S. J. J. B.

Co-ordination and valency. A. A. Blanchard (*J. Chem. Educ.*, 1943, 20, 454—460). L. S. T.

Stereochemistry of co-ordination number eight. Isomerides for the trigonal prism with symmetry C_3^2 . L. E. Marchi (*J. Amer. Chem. Soc.*, 1943, 65, 2257—2258).—The trigonal prism with two extra bonds along the normals to two of the rectangular faces and with symmetry C_3^2 is discussed in respect of compounds showing co-ordination no. 8, and the isomerides for mono- and bi-dentate groups are listed. The nos. of isomerides for class 4AA of the trigonal prism and the dodecahedron are identical. Conclusions regarding the structure of the $[\text{U}(\text{C}_2\text{O}_4)_4]^{4-}$ ion (cf. A., 1943, I, 194) must be altered to include the prism. W. R. A.

Electrical energy of two cylindrical charged particles. G. P. Dube (*Indian J. Physics*, 1943, 17, 189—192).—Using the approx. Debye-

Huckel theory the electrical energy of two cylindrical particles has been worked out. The energy is min. for a certain val. of interparticle distance and this may be important in explaining thixotropic properties. W. R. A.

Statistical mechanics of liquids, and the gas of hard elastic spheres. O. K. Rice (*J. Chem. Physics*, 1944, 12, 1—18).—General principles are formulated for a model of the liquid state. A gas of hard elastic spheres has a "communal entropy" $3R$ per mol., fully excited in each direction of space, arising from sharing of the available space by all the atoms. The geometry, equation of state, and partition function for an assemblage of hard elastic spheres are considered, and a partition function for a monat. liquid is derived, consisting of terms representing vibrational motion in terms of the Debye characteristic temp. of the solid, and a translational term. Each term contributes to the communal entropy. L. J. J.

Surface tensions and parachors of methyl- and ethyl-amines. E. Swift, jun. and C. R. Calkins (*J. Amer. Chem. Soc.*, 1943, 65, 2415—2417).—Vals. of γ , accurate to 0.5%, are given for mono-, di-, and tri-methyl- and -ethyl-amines at 15°, 25°, and 35°. Parachors show no structural abnormalities in the liquid state. W. R. A.

III.—CRYSTAL STRUCTURE.

Chemistry of oriented growth of crystals of organic compounds.

II. Significance of the hydrogen bond for production of oriented growth of organic compounds. J. Willems (*Naturwiss.*, 1943, 31, 232—233).—A no. of cases of oriented growth of crystals seem to depend on the existence of a H bond between the O of the substance and that of the material on which the crystal is grown. Thus, 1 : 2 : 4- $C_6H_5(OH)_3$, p - $C_6H_4(N-OH)_2$, and 2 : 5- $C_6H_3Cl_2C(OH)_2N-OH$ on the (100) face of calcite and related carbonates, α -quinol, and p - $NH_2C_6H_4CO_2H$ on the (010) face of gypsum, and $(CH_3CO_2H)_2$ on talc, show the effect. C_6Cl_5OH (I) grows from C_6H_5 solution in needle-shaped crystals on the (100) face of $CaCl_2$, $NaCl$, KCl , KBr , $RbBr$, and NH_4Cl , oriented either parallel to the edges or along the diagonals of the face. C_6Br_5OH grows similarly on $NaCl$ and KCl . A linking of the two lattices by a H bond between the O of the phenol and the Cl of the halide is to be expected; it can only be weak. C_6Cl_5 does not orient itself in the same way on $NaCl$ although formally similar to (I); this indicates that the H atom is responsible for the orientation. Orientation of the (I) lattice has also been obtained on carbonates of the calcite series, $NaNO_3$, $KClO_3$, gypsum, anhydrite, Sb_2S_3 , various micas (e.g., muscovite and phlogopite), chlorites (e.g., pennine), sulphanilamide, sulphanilic acid, and sucrose. A. J. M.

X-Ray patterns of hydrated calcium silicates. H. F. McMurdie and E. P. Flint (*J. Res. Nat. Bur. Stand.*, 1943, 31, 225—228; cf. A., 1939, I, 154).—X-Ray diffraction data for powder samples of seven natural and eight synthetic hydrated Ca silicates are recorded. J. W. S.

Crystal structure of boron carbide. H. K. Clark and J. L. Hoard (*J. Amer. Chem. Soc.*, 1943, 65, 2115—2119).—X-Ray investigation of B carbide confirms the data of Shdanov and Sevastianov (A., 1943, I, 82) and yields for the rhombohedral lattice const. a 5.19 Å, α 66° 18', space-group D_{3h}^{12} — $R\bar{3}m$, 3 B_4C mols. per unit cell. Corresponding hexagonal lattice const. are a 5.60, c 12.12 Å, 9 mols. per unit cell. Structural units are a linear chain of 3 C with 12 B arranged at the vertices of a nearly regular icosahedron and distributed formally in an approx. $NaCl$ structure. Each B has 6-fold co-ordination and is approx. at the centre of a pentagonal pyramid. Each B is bonded to 5 others in the same icosahedral group and also to either a C in $2c$ (B in $6h_1$) or a B in $6h_2$ in an adjacent icosahedron (B in $6h_2$). There is, therefore, a continuous three-dimensional network of B throughout the crystal, which accounts for the great hardness and electrical conductivity of B_4C . The apparent existence of room in the structure for more atoms explains why commercial B_4C , having a B/C ratio >4 , is a solid solution. W. R. A.

X-Ray pattern of boron carbide. N. G. Sevastianov (*Zavod. Lab.*, 1939, 8, 1317—1318).—In the system B—C only one carbide, B_4C , is formed. The spacing 3.39 Å. is due to contamination by graphite. J. J. B.

Crystal chemical studies of the alums. V. Gallium alums. H. P. Klug and G. L. Kieffer (*J. Amer. Chem. Soc.*, 1943, 65, 2071—2072). Lattice const. and vals. of ρ from X-ray data have been determined at 25° for $M(Ga)(SO_4)_2 \cdot 12H_2O$ ($M = NH_4, K, Rb, Cs, Tl$). The Cs and Tl alums have the β structure; the others have the α structure. W. A.

Crystal structure of $LaAl_2$. G. E. R. Schulze (*Z. Krist.*, 1942, 104, 257—260).— $LaAl_2$ is a typical cubic Laves phase having the $MgCu_2$ (C 15) structure; a 8.115 Å.; ρ 4.76. Intensities in the powder X-ray diagram are tabulated. A. J. E. W.

Co-ordination of starch in the starch-iodine complex. IV. X-Ray diffraction of butanol-precipitated amylose. R. E. Rundle and F. C. Edwards (*J. Amer. Chem. Soc.*, 1943, 65, 2200—2203).—Diffraction

patterns from wet and dried BuOH-pptd. amylose confirm the helical starch chain with a helix diameter of ~ 13.7 Å., a length per turn of ~ 8 Å., and 6 glucose residues per turn. The helices approximate to a close-packed arrangement in both wet and dried ppts., with alternate helices directed in opposite directions and the probable space-group $D_4^{12}P2_12_1$. Spatial relations between the starch-I complex (I) and dried BuOH ppt. confirm that the I in (I) occupies the interior of the helix. It is suggested that BuOH in the BuOH-pptd. amylose also occupies the interior of the helix. The cell previously reported for (I) (A., 1944, I, 5) must be a pseudo-cell with only pseudo-hexagonal symmetry. W. R. A.

X-Ray fibre pattern from amylose with a glycerol plasticiser. R. E. Rundle and L. W. Daasch (*J. Amer. Chem. Soc.*, 1943, 65, 2261—2262).—The fibre spacing in an amylose with a glycerol plasticiser is 7.5 Å., compared with 10.6 Å. for "B" starch. This indicates a flexibility of the starch chain not found in the cellulose chain. The ascertained spacing suggests that the chains are extended linearly, but they must be folded to account for the spacing. W. R. A.

Molecular structure of fibres made from native egg-albumin. K. J. Palmer and J. A. Galvin (*J. Amer. Chem. Soc.*, 1943, 65, 2187—2190).—Fibres were made from native egg-albumin by complex formation with detergent and drawing under steam. They are composed of parallel bundles of polypeptide chains, having a β -keratin structure, running parallel to the fibre axis. The tensile strength depends on the degree of mol. orientation and can be as high as 38,000 lb. per sq. in. W. R. A.

Electron beam interferences from molten alloys. R. Glocker and H. Richter (*Naturwiss.*, 1943, 31, 236).—Liquid binary alloys give two types of electron interference pattern: (a) superposition of the interference systems of the two components (immiscibility in the liquid state), and (b) occurrence of a new interference pattern (due to miscibility). In the case of Sn—Bi the curve of electron density for the strongest innermost interferences against at. concn. of Bi is linear. Vegard's additive rule for mixed-crystal formation in the solid state can therefore also be applied to the liquid state. The equilibrium diagram for this system in the solid state does not show continuous mixed-crystal formation, such as is indicated for the liquid state by the density-concn. curve. A. J. M.

Variations with temperature of optical properties of conline hydrochloride crystals. J. Jaffray (*Compt. rend.*, 1942, 215, 489—491; cf. A., 1942, I, 231).—Data are recorded for the temp. variation (0—50°) of the λ at which the crystals become uniaxial, and for the λ and temp. variations of the birefringence of plates cut parallel to g^1 , and of the external angle between the optic axes. A. J. E. W.

Retrograde transformation. III. A. Smits (*Z. physikal. Chem.*, 1941, B, 49, 126—130).—In the retrograde transformation tetragonal-cubic observed with ND_4Br , increase of pressure decreases the temp. range of existence of the tetragonal modification. The possible forms of the pseudobinary (T, x) diagram and the corresponding unary (p, T) diagram are discussed theoretically. Two cases are outlined, in which the region of coexistence of the two phases is either open or closed by a crit. max. (Cf. A., 1942, I, 139.) J. F. H.

Thermal analysis in the heated microscope. III. Polymorphic and isomorphous phenomena with s -trinitrobenzene, picric acid, and 2 : 4 : 6-trinitrotoluene. A. Kofler (*Z. physikal. Chem.*, 1941, A, 188, 201—228).—Besides the stable form (m.p. 123.5°), s - $C_6H_3(NO_2)_3$ (I) exists in unstable enantiomorphous modifications of m.p. 106° and 110°, with transition point 85°. Picric acid (II) occurs in stable (m.p. 122°) and unstable (m.p. 75°) forms isomorphous with the forms of (I) of m.p. 110° and 123.5°, respectively. 1 : 2 : 4 : 6- $C_6H_2Me(NO_2)_3$ (III) occurs in one form only. (I) shows complete miscibility with (II), but in the systems of (III) with (I) or (II) there are several crystallographically distinct mixed crystal series. J. W. S.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Magnetic studies on permanganates. A. Mookherjee (*Proc. Indian Assoc. Cult. Sci.*, 1943, 26, 8—9).—Consideration of the effect of the electric field surrounding the MnO_4^- ion in $KMnO_4$ and $Ba(MnO_4)_2$ shows that the paramagnetism of these compounds arises from the high-frequency portion of the orbital moment. Comparison with $K_3Fe(CN)_6$ and the small anisotropy (0.07) support this view. W. R. A.

Magnetic properties of iron included in active charcoals. C. Courty (*Compt. rend.*, 1942, 215, 461—463; cf. A., 1938, I, 321).—Data are recorded for χ (−0.157 to +5.087) and the Fe_2O_3 content (0.0021—0.0152%) of four activated and one unactivated coconut shell charcoals. The contained Fe_2O_3 has an effective χ val. of $+15,000 \times 10^{-6}$ (pure Fe_2O_3 , $+68,000 \times 10^{-6}$). A. J. E. W.

Magnetic susceptibility of iron tetracarbonyl. H. G. Cutforth and P. W. Selwood (*J. Amer. Chem. Soc.*, 1943, 65, 2414—2415).—

The magnetic susceptibility, χ , $\text{Fe}_3(\text{CO})_{12}$ (I), at room temp., when corr. for ferromagnetic impurity, is -0.07×10^{-6} . On keeping in the dark (I) undergoes a slow change, and χ increases.

W. R. A.

Complex ions. VI. Magnetic moments of ferric complex ions. B. Werbel, V. H. Dibeler, and W. C. Vosburgh (*J. Amer. Chem. Soc.*, 1943, **65**, 2329—2334).—The magnetic moment, μ , of Fe^{III} has been determined in aq. $\text{Fe}(\text{ClO}_4)_3$ containing various complex-forming anions. When $[\text{HClO}_4]$ is $> 0.1\text{M}$, $\mu = 5.93 \pm 0.01$, which agrees well with the theoretical spin moment, $\mu = 5.92$. Low vals. of μ , observed when $[\text{HClO}_4]$ is $< 0.1\text{M}$, are attributed to the presence of $[\text{FeOH}]^{2+}$. μ remains unchanged when $\text{C}_6\text{O}_4^{4-}$, 8-hydroxyquinoline-5-sulphonate, Cl^- , CNS^- , and dichloroacetate complexes are formed. μ has lower vals. in OAc^- , chloroacetate, HPO_4^{2-} , $\text{P}_2\text{O}_7^{4-}$, lactate, tartrate, citrate, and aminoacetate complexes. Variation of μ in the latter group with concn. of excess anion and pH indicates the existence of > 1 complex.

W. R. A.

Magnetic susceptibility of cobaltous complexes and their constitution. P. Ray and S. P. Ghosh (*J. Indian Chem. Soc.*, 1943, **20**, 323—328).—The magnetic moments of the central Co atoms in diaquo- Co^{II} , ethylenediaminebisacetylacetonate, Co^{II} -ethylenediguanidium sulphate, -diguanidinium sulphate and hydroxide show that these complexes are of the penetration type. The average moment is 2.66 Bohr magnetons, which is slightly $<$ that calc. on the supposition that the orbital moments are not quenched but are free to orient independently. The discrepancy suggests that the quenching is incomplete.

C. R. H.

Magnetic measurements on catalytically active substances.—See A., 1944, I, 109.

Effect of torsional vibrations on the Barkhausen effect. K. M. Koch (*Naturwiss.*, 1943, **31**, 233—234).—If a stretched Fe wire, magnetised longitudinally, is twisted, the longitudinal component of the magnetisation decreases. This can be demonstrated by surrounding the wire with a coil, amplifying the induced current, and passing it into a loud-speaker. A note of the frequency of the torsional vibration is heard. If the magnetisation is changed during the vibration, the frequency of the note is doubled while the magnetisation is changing, but reverts to the original when it becomes const. If the wire is not vibrating and the magnetisation is altered, the normal Barkhausen noise is heard. If the wire is now slowly set into torsional vibration, the Barkhausen effect gives place to a note of double the vibrational frequency. The effect is well shown by means of an oscillograph.

A. J. M.

Specific heats at low temperatures of hydrates of magnesium chloride. K. K. Kelley and G. E. Moore (*J. Amer. Chem. Soc.*, 1943, **65**, 2340—2342).—Sp. heat measurements on the mono-, di-, tetra-, and hexa-hydrates of MgCl_2 at 52—298° K. are recorded. An anomaly is found for the hexahydrate with a peak at 136.7° K. Calc. entropies at 298.16° K. are 32.8 ± 0.5 , 43.0 ± 0.5 , 63.1 ± 0.7 , and 87.5 ± 1.0 g.-cal. per degree per g.-mol. Free energies of formation of the hydrates from the elements and from anhyd. MgCl_2 and liquid H_2O are listed.

W. R. A.

Specific gravity of butadiene. M. R. Dean and T. W. Legatski (*Ind. Eng. Chem. [Anal.]*, 1944, **16**, 7—8).—The d of 99.6 mol.-% $(\text{CH}_2)_2$ over the range 0—140° F. is recorded; the val. of d (60°/60° F.) is 0.6274 ± 0.00010 .

J. D. R.

Viscosity and structure of pure hydrocarbons. H. A. Kierstead and J. Turkevich (*J. Chem. Physics*, 1944, **12**, 24—27).—The fluidity of hydrocarbons can be satisfactorily represented by the expression $Ae^{-E/kT}$. Vals. of the consts. A and E are given for n -paraffins (C_5 — C_{12} , C_{14} , C_{16} , C_{18} , and C_{22}) and 17 aromatic and branched-chain hydrocarbons. The effect of structure on the vals. of these consts. is discussed.

L. J. J.

Equation of diffusion in a turbulent medium. W. G. L. Sutton (*Proc. Roy. Soc.*, 1943, **A**, 182, 48—75).—A mathematical investigation of the two-dimensional form of the equation of diffusion is presented. The results are applied to the theory of evaporation into a turbulent medium.

G. D. P.

Evaporation from a plane, free-liquid surface into a turbulent air stream. F. Pasquill (*Proc. Roy. Soc.*, 1943, **A**, 182, 75—95).—Experimental investigation of the rate of evaporation from a plain liquid surface into a tangential air stream demonstrates the importance of the type of boundary layer flow. In the case of turbulence the results are in agreement with a theory due to Sutton (cf. B., 1935, 1), a generalisation of which is developed. Applied to the analogous process of the turbulent diffusion of heat in the boundary layer, substantial verification of the theory is obtained.

G. D. P.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Growth of crystals from solution. E. Hofer (*Z. physikal. Chem.*, 1941, **A**, 188, 265—271).—Theoretical. Assuming that the effectiveness of foreign nuclei in causing crystallisation depends on the collecting action of the surface of the heterogeneous particles, the

crystal size should be \propto the square of the concn., in agreement with the author's experimental results (A., 1939, I, 252). A crystal of great solubility will take up more from the mother solution than one of small solubility. The assumption on which these deductions are made, that the concn. gradient in the neighbourhood of the crystal is uniform, is strictly valid only in the special case of the salt in solvents of nearly the same physical properties. The results and deductions support the concept that it is the excess % surface concn. which is effective in causing crystallisation.

J. O'M.-B.

Diffusion thermo-effect. L. Waldmann (*Naturwiss.*, 1943, **31**, 204).—Mathematical. An exact solution of the equation governing the effect is possible for a cylindrical diffusion vessel. The results are quoted.

A. J. M.

Temperature coefficient of diffusion constant of copper in aqueous solutions of sulphuric acid containing copper sulphate. W. A. Patterson and J. T. Burt-Gerrans (*Canad. J. Res.*, 1944, **B**, 22, 5—15).—On the basis of Rosebrugh and Miller's theory of changes of concn. at the electrode (A., 1911, ii, 181), diffusion coeffs. are calc. from the time, t , required for the concn. potential to reach a max., using an oscillograph for time measurements. Use of a new point on the oscillograph potential curve for determining t brings the results into line with those obtained by a different method. Diffusion coeffs. increase linearly with temp. from 10° to 25°, the change being related to the change in η in accordance with the Stokes-Einstein equation.

R. H. F.

Variation in equilibrium pressure of compounds during fusion in the case of miscibility in the solid state. M. Dodé (*Compt. rend.*, 1942, **215**, 436—437; cf. A., 1943, I, 62).—The case is considered in which a solid dissociates into a gas (pressure p) and a second solid, the two solid phases forming an ideal series of mixed crystals. An expression (involving the gradient of the liquidus) giving $d(\log p)/dT$ is derived for the univariant system formed during melting, and possible types of p - T relation are considered.

A. J. E. W.

Energy coefficients of crystalline lattices (VEC) and the structure of binary metallic alloys. O. E. Zvjagintzev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 28—32).—A theoretical treatment of the nature of binary metallic alloys.

L. S. T.

Volume changes in alloys in the heterogeneous solid-liquid range. II. F. Sauerwald (*Metallwirts.*, 1941, **20**, 1211—1213).—Temp.-vol. curves covering the solidification ranges of saturated solutions in the Al-Cu, Al-Zn, Al-Si, Al-Mg, and Mg-Zn systems have been plotted from published data. The results are discussed in relation to conditions when equilibrium is not attained.

C. E. H.

Continuous transition between the daltonide and the berthollide phases in the system iron-nickel-antimony. N. V. Ageev and E. S. Makarov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 20—21).—Results obtained in an experimental investigation of the transition between the berthollide phase of the system Fe-Sb and the daltonide phase of the system Ni-Sb, both with Ni arsenide structure, are presented in the form of a Stokes diagram.

L. S. T.

[Solubility of lithium carbonate.] I. T. Poljanitschka (*Zavod. Lab.*, 1939, **8**, 1052—1054).—1 l. of saturated aq. solution contains at 0° 0.417 and at 100° 0.197 g.-equiv. Vals. are given for the solubility of Li_2CO_3 in salt solutions and 40% EtOH. (See also C., 1944, Part 2.)

J. J. B.

Solubility of carbon as graphite in gamma iron. R. W. Gurry (*Amer. Inst. Min. Met. Eng.*, 1942, *Tech. Publ.* 1440, 7 pp.; *Metals Tech.*, 9, No. 3).—The solubility of graphite in austenite was determined by carburising pure Fe in an atm. of H_2 and PhMe, and determining the C content of the quenched steel at equilibrium. Microscopical examination showed the steel to be free from graphite. The solubility at 957° was 1.39%, and at 1110° was 1.89%. By extrapolation, the max. solubility, at 1135°, is 1.98%.

R. KE.

Determination of ionic adsorption in the Helmholtz-Gouy (electrical) layers by the combination of electrokinetic and interfacial tension measurements. W. Dickinson (*Trans. Faraday Soc.*, 1944, **40**, 48—59).—Data recorded in a previous paper (cf. A., 1940, I, 366) on the effect of KCl, KI, and KCNS on the electrophoretic mobilities of emulsions of cetyl acetate (I) and on the interfacial tension between (I) and the aq. solutions are used to calculate the ionic composition of both the rigid and the mobile parts of the Stern double layer. I^- and CNS^- are strongly positively adsorbed throughout the range of concn. examined (0.01—0.2N.). Cl^- shows slight positive adsorption below 0.05N. and slight negative adsorption at higher concns. K^+ from KI and KCl is negatively adsorbed, and the surface excess of K^+ from KCNS is ~ 0 , over the whole concn. range.

F. L. U.

Density of dilute solutions of strong electrolytes. F. Sauter (*Z. physikal. Chem.*, 1941, **A**, 188, 229—234).—A general relationship between the d and osmotic pressure of a solution is derived and is applied to dil. solutions of strong electrolytes. This leads to a correction of the formula of Redlich and Rosenfeld (A., 1931, 906).

J. W. S.

New group of colloidal electrolytes. N. R. Dhar and S. Ghosh (*J. Indian Chem. Soc.*, 1943, 2, 282—288).—Observations on Λ and on pptn. by electrolytes in absence of alkali or in presence of traces of alkali indicate that sols of HSbO_3 , HVO_3 , H_2MoO_4 , and H_2WO_4 are typical colloidal electrolytes. F. J. G.

Sedimentation volumes and rigidity in suspensions of sodium soaps in mineral oils. W. Gallay and I. E. Puddington (*Canad. J. Res.*, 1944, B, 22, 16—20).—The sedimentation vol. of Na soaps increases with temp. and with decreasing viscosity index of the oil. Large sedimentation vol. is due to attraction between particles resulting in a scaffolding structure. Flow measurements on such suspensions show the existence of a yield point, indicating rigidity of the suspension. R. H. F.

Stress-strain data for vulcanised rubber under various types of deformation. L. R. G. Treloar (*Trans. Faraday Soc.*, 1944, 40, 59—70; cf. A., 1944, I, 15).—Data are recorded for two types of vulcanised rubber under (a) two-dimensional extension, (b) simple elongation, (c) pure shear, and (d) combined elongation and shear. Comparison with the theoretical relations based on the mol. network model shows good agreement for (a), less good for (b) and (c). The effect of (d) is accounted for satisfactorily. The theory provides a satisfactory explanation of rubber-like elasticity, and a useful basis for the description of the mechanical properties of rubber under large deformations of any type. F. L. U.

Anomalous viscosity and flow-birefringence of protein solutions. I. General behaviour of proteins subjected to shear. A. S. C. Lawrence, J. Needham, and S. C. Shen. II. Dilute solutions of proteins from embryonic and other tissues. A. S. C. Lawrence, M. Miall, J. Needham, and S. C. Shen (*J. Gen. Physiol.*, 1944, 27, 201—232, 233—271).—I. Viscometric methods of investigating the shape of protein particles are discussed. The application of a new viscosimeter (cf. C., 1944, Part 2) to the measurement of relative and anomalous η and of flow-birefringence of dil. protein solutions is described. The general behaviour of protein solutions subjected to shear is summarised.

II. Examination of a no. of proteins suggests that they can be conveniently classified into four groups. Group A consists of proteins which show flow anomaly both in bulk and in the surface film with flow-birefringence, and which are fibrillar in bulk and in film, e.g., tobacco mosaic virus, myosin. Groups B₁ and B₂ consist of proteins which show flow anomaly in film but not in bulk and no flow-birefringence in the bulk phase. In bulk the particles are spherical but are fibrillar in film. B₁ proteins show flow anomaly immediately after formation, e.g., mammalian serum-euglobulin and -pseudoglobulin, avian ovoglobulin, amphibian embryo-euglobulin b, and, possibly, plasmosins. B₂ proteins show flow anomaly only after an interval, e.g., cryst. avian ovalbumin, amphibian embryo-pseudoglobulin. Group C consists of proteins which show flow anomaly neither in bulk nor in film, e.g., cryst. insulin and methæmoglobin, amphibian embryo-euglobulin c, amphibian egg-jelly-mucoprotein, human umbilical cord-mucoprotein. The theoretical significance of fibrillar proteins is discussed in relation to experimental morphology and cytology. A bibliography of 262 references is appended. C. R. H.

Yeast-ribonucleic acid. VII, VIII.—See A., 1944, II, 112.

VI.—KINETIC THEORY. THERMODYNAMICS.

Equilibrium composition of gaseous mixtures under high pressure. A. I. Brodski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 237—238).—Theoretical. The activity coeffs. of the components of a compressed gaseous mixture are given by $\log f_1 = 9/128 \cdot \pi_1/\theta_1 \cdot (1 - 6/\theta_1^2)$, where π_1 and θ_1 are reduced pressures and temp. F. J. G.

Second dissociation constant of phenol-*p*-sulphonic acid and the pH values of phenolsulphonate-chloride buffers from 0° to 60°. R. G. Bates, G. L. Siegel, and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1943, 31, 205—223).—From e.m.f. measurements on cells containing H. and Ag-AgCl electrodes in the presence of various concns. of $p\text{-OH-C}_6\text{H}_4\text{SO}_3\text{H}$ (I), NaOH, and NaCl the thermodynamic dissociation const. of the OH-group of (I) has been measured at 0—60° as $pK_a = 1961.2/T - 1.1436 + 0.012139T$. Formulae relating ΔG° , ΔH° , ΔS° , and ΔC_p with T for this dissociation are deduced. At 25° these quantities have the vals. 12,351 and 4036 g.-cal., and -27.9 and -33 g.-cal. per degree per g.-mol., respectively. The pH vals. of solutions containing various ratios of uni- to bi-valent ion ($\frac{1}{2}$ —1) at various temp. are recorded. These are suitable buffer solutions for the pH range 8.6—9.0. J. W. S.

Potentiometric determination of solubility product. R. Nasänen (*Z. physikal. Chem.*, 1941, A, 188, 272—283).—The theory of pptn. titrations is examined and an equation for the difference between the end-point and the inflexion on the titration curve is deduced. This is experimentally determined by reference to the alkalimetric determination of Mg and depends only on the val. of m and n in the pptd. A_mB_n . The solubility product can be determined from the min. of the buffer capacity curve. The concn. solubility product

of $\text{Mg}(\text{OH})_2$ is determined at the min. p.d. for different KCl concns. For the thermodynamic solubility product the val. of 3.07×10^{-11} is obtained so that this electrolyte obeys the Debye-Hückel theory. The results here reported are > those in the literature, but the latter are not const., owing perhaps to the carbonate content of the solutions and to the solubility of the glass vessel. The latter does not affect the present method owing to the short duration of the experiments. J. O'M.-B.

Solidification point curves of binary [fatty] acid mixtures. III. Tetracosanoic to triacontanoic acids. H. A. Schuette, R. M. Christenson and H. A. Vogel (*Oil and Soap*, 1943, 20, 263—265; cf. B., 1940, 222; A., 1941, I, 35).—The solidification point (s.p.) diagrams (and tabulated experimental figures) for binary mixtures of synthetic tetracosanoic (s.p. 83.82°, 83.45°), hexacosanoic (s.p. 87.38°, 87.06°), octacosanoic (s.p. 90.48°), and triacontanoic acids (s.p. 93.10°) are presented. Starting with erucic acid, which was reduced and converted into Et behenate, each homologue was successively synthesised by reducing the ester to the corresponding alcohol, converting this into the iodide, and interaction with malonic ester; the prep. of triacontanoic acid from Et octacosanoate is described in detail. Attempts to separate the fatty acids of Chinese insect wax into binary mixtures by fractional distillation of the Et esters with a Widmer column were unsuccessful. E. L.

Salting-out effect. T. J. Morrison (*Trans. Faraday Soc.*, 1944, 40, 43—48).—The salting-out of PhOH , $\text{CH}_3\text{PhCO}_2\text{H}$, and BzOH in aq. solution by some uni-univalent electrolytes has been investigated over a range of temp. and for various concns. (c) of electrolyte. The results are tabulated. Factors that determine the temp. variation of solubility are predominant in determining the variation in salting-out effect. If c is in mols. per 1000 g. of H_2O , the data are better expressed by $\log s_0/s = k_1 c^\beta$ than by $\log s_0/s = k c$, s_0 and s being the solubilities in H_2O and salt solution respectively. Both k_1 and β vary with temp. F. L. U.

Effect of the physical state of the solid reactants on the equilibrium $\text{Fe/Fe}_2\text{O}_3$ with $\text{H}_2\text{O/H}_2$. R. Fricke, K. Walter, and W. Lohrer (*Z. Elektrochem.*, 1941, 47, 811).—Use of a better val. for the heat of formation of Fe_2O_3 at room temp. does not influence the conclusions made in a previous paper (A., 1944, I, 37). J. F. H.

Structure and composition of the double carbides of the system W-Co-C determined from the relative intensity of Debye lines. E. N. Kisliakova (*J. Phys. Chem. Russ.*, 1943, 17, 108—114).—The system W-Co-C shows two distinct phases, with compositions near $\text{W}_2\text{Co}_2\text{C}$ (spacing 11.19 Å.) and $\text{W}_4\text{Co}_4\text{C}$ (spacing 10.89 Å.), the unit cell of which contains 96 metal atoms. J. J. B.

Spectroscopic determination of the heat of association of methyl alcohol in CCl_4 . R. Mecke and H. Nückel (*Naturwiss.*, 1943, 31, 248).—Spectroscopic measurements confirm that for normal alcohols in CCl_4 no double mols. are formed ($k_{12} \sim 0$). The mean association const. $k_n = (k_{1n})^{1/(n-1)}$ ($n > 2$) can be taken as independent of n . Vals. for the heat of association per g.-mol. of MeOH in CCl_4 are 4.59 kg.-cal. (10—20°), 4.72 kg.-cal. (20—30°), and 4.82 kg.-cal. 30—40°). J. F. H.

VII.—ELECTROCHEMISTRY.

Conductivity of strong electrolytes. J. Lange (*Z. physikal. Chem.*, 1941, A, 188, 284—315).—The re-evaluated conductivity results for 560 electrolytes are tabulated and shown to conform to a simple relation the coeffs. of which can be calc. from the Debye-Hückel-Onsager theory. The poorest agreement is obtained for non-aq. media and for electrolytes of high valency; the inherent difficulty for the former is the almost unavoidable presence of a trace of H_2O . A new method is given for obtaining the limiting equiv. conductivity from an assumption of the validity of the interionic attraction theory at low concns. Vals. of Λ° are tabulated; they show Walden's rule to be obeyed only very roughly except for large ions. The results are sufficient to prove that the conductivity of strong electrolytes is a function only of the electrostatic forces. J. O'M.-B.

Irreversible electrode potentials of metals. G. B. Clark and G. V. Akimov (*Trans. 2nd Russ. Conf. Corrosion Metals*, 1943, 2, 33—51).—The electrode potential V of Si and 21 metals is determined in 3% NaCl, 0.1N-HCl, 0.1N- HNO_3 , and 0.1N-NaOH 1 and 5 min. after immersion in the stationary electrolyte, when the solution is stirred, and when the electrode is being abraded with a CSi disc. The effect of time and of stirring on V is small, usually 20—70 mv. The effect of abrasion is very large for the elements of the sub-groups a of the periodic system (Be, Mg, Al, Si, Nb, Cr, Mo, and Mn), and V becomes more negative (less noble) by 300—1000 mv.; this is due to destruction of the protective film and increase of the anodic area of the local elements. The V of the transition group (Fe, Co, Ni) is lowered by abrasion by 200—500 mv., and the V of the sub-groups b (Cu, Ag, Au, Zn, Cd, Hg, Tl, Sn, Pb, Sb, and Bi) is lowered by <200 mv. or not at all. The effect of abrasion is small when the cathodic and the anodic areas of an undisturbed electrode have similar magnitudes. J. J. B.

Piezoechemical studies. XXXII. Piezodynamical examination of the Gladstone-Tribe mechanism of the lead accumulator. E. Cohen and G. W. R. Overdijkink (*Z. physikal. Chem.*, 1941, **188**, 316—330).—The pressure coeff. of the e.m.f. of an accumulator is more accurately measurable than the temp. coeff. and is used to determine the chemical reaction taking place in the accumulator. The val. obtained agrees closely with that derived from the vol. contraction which takes place on working, assuming the equation of the theory, which is hence considered verified. J. O'M.-B.

Anodic passivation of lead in sulphuric acid. B. N. Kabanov (*Trans. 2nd Russ. Conf. Corrosion Metals*, 1943, **2**, 67—85).—The anodic overvoltage η on Pb in H_2SO_4 slightly increases with c.d. and with concn. of H_2SO_4 (2—13*N.*) and is lowered by a temp. increase (—35° to 45°). PhOH raises and gelatin lowers it. At c.d. of 10^{-6} to 10^{-3} amp. per sq. cm. η — const. + 0.18 log c.d., and the η is due to a supersaturation of PbSO_4 caused by the slowness of its crystallisation. At c.d. > 0.03 amp. per sq. cm. η increases linearly with c.d. and is due to a retardation of the ionisation of Pb. Müller's theory of the passivity of Pb is not correct as the ohmic resistance of the electrolyte layer at the electrode is ~0.01 of that postulated by Müller. The extent of covering of Pb by PbSO_4 is determined by measuring the capacity of the electrode in the course of its passivation. The charge Q required to raise the potential of Pb by 0.1—0.2 v. is the larger the more dil. is H_2SO_4 and the higher is the temp., and $Q \propto (\text{c.d.})^{-0.1}$ to $(\text{c.d.})^{-0.4}$. If c.d. varies during the polarisation, Q depends only on the average c.d. EtOH reduces Q , gelatin and methylene-blue raise it. These results are accounted for by the proportionality between Q and the thickness of the passivating PbSO_4 layer; this thickness increases with the solubility and the rate of diffusion, and when the rate of crystallisation is lowered. Equations for the rate of growth of the passivating layer are derived. J. J. B.

Theory of passivity phenomena. XXXIII. Connexion between anodic behaviour of iron and corrosion accompanying potential oscillations in chromic acid-sulphuric acid solutions. W. J. Müller and E. Löw (*Z. physikal. Chem.*, 1941, **A**, 189, 70—87).—Fluctuations of potential occurring when Fe is immersed in H_2CrO_4 - H_2SO_4 mixtures can be explained by supposing that passivity is due to a surface film. The connexion between passivity and anodic oxidation indicates that potential fluctuations can occur only when the surface is covered with a film of oxide. In anodic oxidation, passivity depends on c.d. When high c.d. is used the pores in the surface are covered with a film of oxide. The time elapsing before the sudden decrease in current occurs is the smaller the larger is the initial c.d. This passivation time also depends on the diffusion of H_2CrO_4 into the neighbourhood of the electrode. The passivation time is short with high $[\text{H}_2\text{CrO}_4]$, with unprotected electrodes, and particularly if the electrodes are immersed after the circuit has been closed, even if the c.d. is low. The potential fluctuation is due to the fact that after the decrease of the current, the surface film is dissolved by the H_2SO_4 . The fluctuations vary with $[\text{H}_2\text{CrO}_4]$ and in presence of $\text{N-H}_2\text{SO}_4$ occur with concns. of H_2CrO_4 between 2 and 7%. The fraction of free surface of Fe when potential oscillations occur is ~0.001; this increases with increase of passivation time. A. J. M.

Passivity of platinum. B. V. Erschler (*Trans. 2nd Russ. Conf. Corrosion Metals*, 1943, **2**, 52—66).—Earlier results (cf. A., 1941, **I**, 470) are reviewed. J. J. B.

Mechanism of the depolarisation of local cathodes in corrosion involving oxygen depolarisation. N. D. Tomashev (*Trans. 2nd Russ. Conf. Corrosion Metals*, 1943, **2**, 11—32).—The current strength between a Zn plate and a smaller Cu plate in 0.5*N.*-NaCl, measured at various areas f of the Cu plate, is $I = k(2.25\sqrt{f} + f/\delta)$, k being a const. which can be calc. from the diffusion coeff. of O_2 , and δ the thickness of the diffusion layer. Experiments give $\delta \sim 1$ mm. Only at $f > 6$ sq. cm. is $I \propto f$. If a Cu plate and a Zn ring surrounding it in the horizontal plane are covered with a layer, d cm. thick, of 3% NaCl, I has a sharp max. at $d = 0.05$ mm.; at lower d vals. I is smaller because of the increased ohmic resistance, and at higher d because of the longer diffusion path for O_2 ; at $d > 1$ mm. I is independent of d . I is raised by agitating the air above the NaCl solution. The term $2.25\sqrt{f}$ is due to the c.d. being larger near the edge of the cathode. Measurements of I between a Zn plate and a set of concentric Cu rings show that the c.d. 0—0.5 mm. from the edge is 4.5 times that in the centre of the cathode. If, at a const. f , the cathode consists of several spots instead of one plate, I in 3% NaCl is increased since the cross-section of the diffusion path for O_2 is raised, but the difference is negligible in N-HCl , in which H_2 is evolved. If the layer of 3% NaCl covering the cathode is < 1 mm. thick, the difference between a single and a composite cathode is reduced. If d is larger, an increase of the f of the composite cathode (or of the amount of cathodic inclusions in a corroding metal) does not cause a marked increase of I , the cross-section of the diffusion path being nearly equal to the total area of the corroding metal independently of the area of the cathodic inclusions. J. J. B.

Capacity of the double electric layer on Wood's metal. S. Karpatshev, N. Ladigin, and V. Zikov (*J. Phys. Chem. Russ.*, 1943, **17**, 75—78).—The capacity was measured directly with a.c. at 50 cycles per sec. At the e.m.f. of $\text{Hg}|\text{HgCl}_2, \text{N-KCl}|\text{Wood's metal} = 1$ v. the capacity in N-KCl had a min.; it was $\sim 15 \mu\text{F.}$ per sq. cm. at 75° (liquid cathode) and $\sim 20 \mu\text{F.}$ per sq. cm. at 65° (solid cathode). It rose to $\sim 100 \mu\text{F.}$ per sq. cm. when the e.m.f. was ~ 0.85 v. J. J. B.

Formation and growth of electrodeposited crystals. K. M. Gorbunova (*Trans. 2nd Russ. Conf. Corrosion Metals*, 1943, **2**, 142—152).—Theories of crystal growth, based on consideration of elementary processes, often fail to agree with the observed rate of growth, since the latter is determined by the conditions of diffusion. Zn was electrodeposited from 4.7*N.*- ZnSO_4 on to various faces of a single Zn crystal. At a const. overvoltage the c.d. on the basis (0001) < prism (1010) < prism (1120); these c.d. are \propto the rate of growth of the crystal face. J. J. B.

VIII.—REACTIONS.

Primary reactions induced by nuclear processes. H. Suess (*Z. Elektrochem.*, 1941, **47**, 765).—A brief summary. J. F. H.

Kinetics and reaction mechanisms. K. H. Geib (*Z. Elektrochem.*, 1941, **47**, 761—765).—An attempt is made to limit the uncertainty of determining reaction mechanisms by recourse to theoretical considerations. The mechanism of several reactions is discussed on the basis of mol. structure and the principle of least motion, formulated by Rice and Teller (*A.*, 1938, **II**, 425). J. F. H.

Chemical kinetics and the second law. E. Baur (*Z. Elektrochem.*, 1941, **47**, 747—749).—A brief discussion of partial equilibrium and anti-catalysis. J. F. H.

Calculations of velocity coefficients from experimental data. J. A. Christiansen (*Z. physikal. Chem.*, 1941, **A**, 189, 126—134).—The weighting of different results in a series of determinations in kinetic experiments is discussed. The assumption is made that the wts. should be so chosen that the sum of the squares of the deviations, $\Sigma(D_{\text{min.}}^2)$, should be equal to the sum of the squares of the errors in reading, $\Sigma(\delta x)^2$. The mean val. of k is readily calc. from the individual vals. from the relationship $k\Sigma G - \Sigma Gk$, where G is the function governing the order of reaction. Tables for G are given for the case of first- and second-order reactions. A. J. M.

Thermal decomposition of higher hydrocarbons. W. Jost and L. von Muffling (*Z. Elektrochem.*, 1941, **47**, 766—773).—The homogeneous thermal decomp. of $n\text{-C}_6\text{H}_{14}$, $n\text{-C}_7\text{H}_{16}$, $n\text{-C}_8\text{H}_{18}$, $\beta\text{-dimethylhexane}$, $\beta\beta\text{-trimethylpentane}$, cyclohexane, PhMe, PhEt, PhPr^a, and PhPr^b was studied by pressure measurements and analysis. No definite conclusions could be reached as to the reaction mechanisms. In the n -paraffins, addition of $\cdot\text{CH}_3\cdot$ approx. doubles the rate of decomp. Increased chain branching leads to greater quantities of H_2 and C_1 , C_2 and higher fractions, but less C_2 fraction. Addition of HgMe_2 accelerates the rate of pressure increase owing to the extra Me radicals produced. One Me radical decomposes 1.5—2 mols. of paraffin. Increase of side-chain in the C_6H_5 derivatives by $\cdot\text{CH}_2\cdot$ approx. doubles the rate of decomp. J. F. H.

Homogeneous thermal decomposition of cyclohexane and methylcyclohexane. G. R. Schultze and (Frl.) G. Wassermann (*Z. Elektrochem.*, 1941, **47**, 774—778).—Preliminary. The thermal decomp. of cyclohexane (I) and methylcyclohexane (II) was investigated at temp. up to 550° and at initial pressures of 100—400 mm. The primary reaction is of the first order; for (I), $\log k = -64,100/2.3RT + 13.8$; for (II), $\log k = -57,900/2.3RT + 12.65$. Both decomps. are preceded by an induction period, which is more marked with (I); no further evidence of a chain reaction was found. Approx. $-\Delta G$ vals. for some of the possible reactions were calc. J. F. H.

Kinetics of ring polymerisation. XII. Explosive polymerisation reactions. G. V. Schulz and F. Blaschke (*Z. Elektrochem.*, 1941, **47**, 749—761).—Polymerisation of $\text{CH}_3\cdot\text{CMe}\cdot\text{CO}\cdot\text{Me}$ in presence of O_2 or peroxides occurs with a steady increase in reaction velocity, until, after induction periods (τ) of varying length, the unused monomer reacts violently with an increase in temp. (up to 90°). τ may last several hr., and is the smaller the higher is the temp. Measurements of composition, degree of polymerisation, viscosity, and temp. during the reaction show that the explosiveness of the reaction is caused by chain-branching. J. F. H.

Kinetics of formaldehyde-phenol condensation. H. von Euler and S. von Kispeszy (*Z. physikal. Chem.*, 1941, **A**, 189, 109—121).—The reaction of xylenol with CH_2O in acid and in alkaline solution has been investigated. The $[\text{CH}_2\text{O}]$ in the supernatant liquid was determined from time to time by pptn. as the trinitrophenylhydrazones, treating the ppt. with NaOH in EtOH, and determining the coloured compound formed by means of a photometer. The reaction is approx. bimol. For the condensation of *o*-4-xylenol (I)

with CH_2O , k is ~ 124 , and for the *o*-3-compound it is 110 in either acid or alkaline solution. k for PhOH in place of xyleneol is $\sim 76\%$ greater. In the acid condensation of (I) with CH_2O , xyleneol alcohol is formed. The bromination of various xyleneol derivatives was investigated in order to determine the no. of reactive positions on the xyleneol nucleus. This is $>$ the no. of free *o*- and *p*-positions. Hence the side-chain must also be brominated. A. J. M.

Consecutive competitive reactions. R. M. Fuoss (*J. Amer. Chem. Soc.*, 1943, 65, 2406—2408).—Mathematical. The amounts of the five substances present in the reaction system $\text{AX}_2 \rightarrow \text{RAX}_2 \rightarrow \text{R}_2\text{AX}_2 \rightarrow \text{R}_3\text{AX}_2 \rightarrow \text{R}_4\text{A}$, the reagent in each reaction being RY , have been calc. as functions of the total added RY , and reaction probability ratios. W. R. A.

Chain transfer in the polymerisation of styrene. Reaction of solvents with free radicals. F. R. Mayo (*J. Amer. Chem. Soc.*, 1943, 65, 2324—2329).—Assuming that certain solvents reduce the mol. wt. of polymerising styrene by transferring H or Cl atoms to the growing polymer radicals, a "transfer const." may be defined, which is characteristic of the solvent. Transfer consts. of cyclohexane, C_6H_6 , PhMe , PhEt , and a $\text{C}_6\text{H}_4\text{Et}_2$ have been calc. and quantitatively support the theoretical development. The coexistence of transfer between polymer radicals and both polymer and monomer mols. is suggested. W. R. A.

Formation of chlorate in hypochlorite solutions. H. Ramstetter and G. Hantke (*Z. physikal. Chem.*, 1941, A, 189, 122—125).—In alkaline solution the decomp. of NaOCl at 45° is bimol. In acid solution, the uni- and bi-mol. coeffs. show a decided trend. The formation of ClO_3^- proceeds to completion in slightly alkaline solution but the rate is slow. A. J. M.

Polarographic determination of the velocity coefficients for the oxidation of haem and other ferro-complexes by hydrogen peroxide. R. Brdicka and K. Wiesner (*Naturwiss.*, 1943, 31, 247).—Preliminary. A new explanation of the displacement of the polarographic reduction potential of H_2O_2 by Fe-porphyrin complexes (cf. A., 1937, III, 163) is given. The mechanism involves a cyclic alteration of the valency of Fe; haemin (I) is electrolytically reduced to haem (II), which is then chemically oxidised by H_2O_2 to (I). The process continues until the concn. ratio of (I) and (II) is that required by their redox potential equation. The rate-determining step of the oxidation is $\text{Fe}^{2+} + \text{H}_2\text{O}_2 = \text{Fe}^{3+} + \text{OH}^- + \text{OH}$. An equation is deduced which enables μk to be determined, μ being the thickness of the phase boundary layer and k the velocity coeff. k for α -chlorohaemin determined in this way is $2 \times 10^7 \text{ sec}^{-1} \text{ g.-mol./l.}$ J. F. H.

Oxidation of oxalic acid solutions by elementary oxygen in the presence of manganese. (Fr.) K. von Baczko and E. Schreier (*Z. Elektrochem.*, 1941, 47, 801—805).—The oxidation of $\text{H}_2\text{C}_2\text{O}_4$ by gaseous O_2 in aq. H_2SO_4 in the presence of MnSO_4 was studied at various concns. of reactants and at temp. 100—118°. Typical chain phenomena are observed. A mechanism is proposed in which the Mn^{2+} ions first disproportionate to Mn^{3+} and Mn^+ . The subsequent reactions are: (a) $\text{Mn}^{3+} + \text{HC}_2\text{O}_4 \rightarrow \text{Mn}^{2+} + \text{CO}_2\text{H} + \text{CO}_2$ (start of chain), (b) $\text{CO}_2\text{H} + \text{O}_2 \rightarrow \text{CO}_2 + \text{HO}_2$, $\text{HO}_2 + \text{HC}_2\text{O}_4 \rightarrow \text{CO}_2 + \text{CO}_2\text{H} + \text{HO}_2$ and $\text{HO}_2 + \text{H}^+ \rightarrow \text{H}_2\text{O}_2$ (chains), and (c) $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ (breaking of chain). J. F. H.

Proof of accuracy of hydrodynamic-thermodynamic theory of detonation for solid and liquid explosives. A. Schmidt (*Z. physikal. Chem.*, 1941, A, 189, 88—94).—For solid and liquid explosives the hydrodynamic-thermodynamic theory for the calculation of detonation velocity is difficult to apply owing to the fact that the equation of state of the gases formed is unknown. Using Aberl's modification of van der Waals' equation, $p/d = vRT/(v - nb)$ (p = pressure, $v = 1/d$, n = no. of g.-mols. of gas per kg. of explosive, b = co-vol. of mols.) the following equation was deduced for the propagation velocity D of the wave: $D = \{v/(v - nb)\} \sqrt{\gamma(8.32\gamma n_2 T_2)}$ ($\mu = d$ in wave/d of explosive; $\gamma = c_p/c_v$). The effect of d on detonation velocity was confirmed experimentally. Compressed nitrocellulose has a higher detonation velocity when it contains 20% of H_2O . The explosion temp. is lowered, but the increase in vol. of gas $>$ compensates for this. The detonating power of an explosive can be determined by finding the distance away from another explosive at which it will cause detonation. The detonating power of an explosive decreases with increasing d . This is explained by supposing that the explosion of the first substance produces a compression shock on the surface of the second, and this must be maintained if detonation is to occur. If the d of the second explosive is too high no detonation occurs as the shock is not maintained. A. J. M.

Reaction of 2- α -chloroalkylbenzimidazoles with potassium iodide.—See A., 1944, II, 83, 84.

Philosophy in catalysis, analysis in philosophy. A. Mittasch (*Z. physikal. Chem.*, 1941, A, 189, 44—62). A. J. M.

Possibility of auto-vibrations in a homogeneous chemical system involving a quadratic auto-catalysis. D. A. Frank-Kamenetzki and I. E. Salnikov (*J. Phys. Chem. Russ.*, 1943, 17, 79—86).—Some

conditions under which periodic catalytic reactions can occur are discussed. J. J. B.

Acceleration by iron of reduction by hydrogen peroxide. K. Yamafuji, K. So, and H. Takaishi (*Biochem. Z.*, 1941, 308, 29—36).— H_2O_2 is decomposed with production of reducing activity [shown by Thunberg's methylene-blue (I) method] by aq. suspensions and, to a greater extent, solutions (in 0.1N-NaOH) of haematin. The decomp. of H_2O_2 is also effected by OH^- , but with haematin the amount of H_2O_2 decomposed is much less, and the rate of decolorisation of (I) is greater, than that due to alkali. Absence of air has no effect on the reduction of (I) or decomp. of H_2O_2 . The reducing activity is also produced by inorg. Fe, Fe^{2+} being more active than Fe^{3+} and FeSO_4 than FeCl_3 . Cu^{2+} , which is very active in decomp. H_2O_2 , does not produce reducing activity. Zn haematoporphyrin is inactive. The mechanism of the reducing activity is discussed. F. O. H.

Reaction of sulphur dioxide with olefines. Ceiling-temperature phenomena. R. D. Snow and F. E. Frey (*J. Amer. Chem. Soc.*, 1943, 65, 2417—2418).—Simple olefine hydrocarbons and SO_2 undergo a catalysed reaction in a homogeneous liquid phase to form polysulphones of high mol. wt. but on raising the temp. the reaction is arrested at a characteristic temp. called the "ceiling temp." The characteristic temp. is unaffected by proportions of reactants and by the nature of the catalyst. It is considered that the olefine acts as inhibitor to the reaction and that the ceiling temp. is lowest for olefines most susceptible to acid-catalysed polymerisation. W. R. A.

Activation of aluminium chloride by the catalytic action of chlorides of elements of the fourth group of the periodic classification. E. Ott (*Angew. Chem.*, 1941, 54, 142—144).—A review of published data. The catalytic activity of AlCl_3 for Friedel-Crafts and Gattermann-Koch syntheses, and for reaction of CCl_4 with aliphatic and aromatic hydrocarbons to give polymerisable olefines, can be increased by addition of chlorides of any elements of the 4th periodic group. L. J. J.

Catalytic isomerisation of paraffin hydrocarbons. I. Butanes. P. A. Leighton and J. D. Heldman (*J. Amer. Chem. Soc.*, 1943, 65, 2276—2280).—The homogeneous liquid-phase isomerisation of $n\text{-C}_4\text{H}_{10}$, catalysed by $\text{AlBr}_3\text{-HBr}$ mixtures, has been studied. Anhyd. AlBr_3 has no catalytic action, but traces of moisture induce catalysis; HAlBr_4 is regarded as the true catalyst. ΔE of activation of isomerisation of $n\text{-C}_4\text{H}_{10}$ is 9.2 kg.-cal. per mol. The calc. temp.-independent rate factor of $10^{8.4}$ is \ll that predicted from collision rate considerations. W. R. A.

Kinetics of enzyme-substrate compound of peroxidase.—See A., 1944, III, 284.

Peroxy-compounds of quinquivalent vanadium and their action as active intermediates in the catalytic decomposition of hydrogen peroxide. K. F. Jahr (*Z. Elektrochem.*, 1941, 47, 810).— V^{5+} reacts with H_2O_2 to give two peroxy-compounds, which in solution enter into the equilibrium: $[\text{VO}_2] \cdot \text{aq.}]^{++} + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightleftharpoons [\text{VO}_2(\text{O}_2)] \cdot \text{aq.}]^{++} + 6\text{H}^+$. In solutions not strongly acid the anion of the diperoxyvanadic acid (I) is formed. Hydrated V_2O_5 dissolves in aq. H_2O_2 to give (I). This decomposes with evolution of O_2 , forming orthovanadic acid, which in presence of H^+ ions finally gives pentavanadic acid. Octavanadic acid is formed as an unstable intermediate, which is very active as a catalyst for the decomp. of H_2O_2 . J. F. H.

Catalytic investigation on alloys. X. Catalytic activity of alloys of copper with nickel, palladium, and platinum. G. Rienacker (*Z. Elektrochem.*, 1941, 47, 805—809).—The catalytic action of alloys of Cu with Ni, Pd, and Pt on the dehydration of HCO_2H and the hydrogenation of C_2H_4 was studied. Each system forms a continuous series of solid solutions with face-centred cubic lattices. In each case Cu is the least active element. The catalytic properties are not additive. Use of kieselguhr as support increases the activity of the pure components, but not for mixed catalysts. Catalysts with ordered lattices are more effective than disordered types. J. F. H.

Kinetics of the catalytic oxidation of acetylene on active manganese dioxide. V. Roiter and M. Rusov (*J. Phys. Chem. Russ.*, 1943, 17, 87—96).—30—100 l. of air containing 0.04—0.57% of C_2H_2 were passed per 1 hr. through 1 g. of commercial active MnO_2 . The rate v of oxidation was determined from the temp. of the air before and after passing the catalyst; this method was more exact than chemical analysis, provided that the temp. of the catalyst was kept const. by adjusting the temp. of the oncoming air. At 142° $v \propto [\text{C}_2\text{H}_2]$, at 190° $v \propto [\text{C}_2\text{H}_2]^{0.75}$, and at 220° $v \propto [\text{C}_2\text{H}_2]^{0.5}$; at lower temp. it is determined by the rate of reaction, and at higher temp. by the rate of diffusion. At 142° v is nearly independent of the speed of air flow and of the grain size of MnO_2 , but at $220\text{--}250^\circ$ it increases with this speed and the degree of dispersity (1—5 mm.) of MnO_2 . The apparent heat of activation at $<170^\circ$ is 14—23 kg.-cal. per g.-mol. J. J. B.

Kinetics of the hydrogenation of acetylene on palladium. E. Cremer, C. A. Knorr, and H. Plieninger (*Z. Elektrochem.*, 1941, 47,

737—747).—The reaction of $C_2H_2-H_2$ mixtures on Pd as catalyst at room temp. was investigated by measuring (1) the pressure change in the gas vessel, (2) the electrical resistance of the Pd to determine the amount of H_2 in the Pd, and (3) the C_2H_2 concn. by analysis of a sample of gas. The main reaction is $C_2H_2 + H_2 = C_2H_4$. The reaction is autocatalytic, the velocity increasing almost up to complete conversion, due to the decreasing inhibition by the C_2H_2 . The pressure change follows the equation $-dp/dt = k \cdot p_{H_2} / (1 + b'p_A)$, where p_{H_2} and p_A are the pressures of H_2 and C_2H_2 respectively, b' is the adsorption coeff. of C_2H_2 , and k is the velocity coeff. J. F. H.

Palladium-synthetic high polymer catalysts. K. E. Kavanagh and F. F. Nord (*J. Amer. Chem. Soc.*, 1943, **65**, 2121—2125).—Polyvinyl acetate (I) in EtOH and $COMe_3$ is an effective colloidal support for Pd hydrogenation catalysts but the particle size of a polymer can be so large that catalytic activity diminishes. Further, acetals of (I) (a long-chain polyhydroxy linear polymer) in AcOH or dioxan can be used for Pd catalysts. Stability and efficiency of the polymer catalysts are enhanced by the presence of small amounts of H_2O . In the presence of thiophen gum arabic-Pd catalysts are inferior to (I)-Pd. W. R. A.

Magnetic measurements on catalytically active substances. H. Morris and P. W. Selwood (*J. Amer. Chem. Soc.*, 1943, **65**, 2245—2252).—Magnetic susceptibilities at different field strengths and temp. have been measured for catalysts for the hydrogenation of C_2H_4 by Ni-activated Cu, Ni on Mg, and Ni-activated Mo oxide. Ni-activated Cu consists of a continuous series of solid solutions containing 66—92.5% Ni. Thermal deactivation of such catalysts is accompanied by a lowering of the Curie point and indicates diffusion of Cu into the Ni-rich alloys. Thermal deactivation of Ni on MgO is accompanied by a decrease in magnetisation but the Curie point remains unchanged. Poisoning by H_2S , CO, Hg, and Pb affects only a small fraction of the Ni atoms presumably on the surface of active microcrystals. Ni-activated Mo oxide contains no metallic Ni. W. R. A.

Catalytic agents for synthesis of carbon disulphide.—See B., 1944, II, 61.

Theory of passivity phenomena. XXXIII.—See A., 1944, I, 105.

Electrolytic reduction of amides.—See B., 1944, II, 61.

Photochemical oxidation-reduction of carbon monoxide and water to carbon dioxide and hydrogen. W. Seitz (*Biochem. Z.*, 1941, **308**, 103—108; cf. A., 1938, I, 315).—When CO in H_2O is strongly illuminated (temp. $>30^\circ$) the reaction $CO + H_2O = CO_2 + H_2$ occurs. Similar reactions occur with CO in EtOH, MeOH, or $COMe_3$. The CO_2 produced is determined by fixing with alkali and titrating. The H_2 produced decolorises H acceptors, e.g., methylene-blue; CO_2 , N_2 , and, in absence of CO, H_2 do not cause decolorisation. In neutral solution, illumination and presence of basic or buffered acid H acceptor are necessary for the reaction but in slightly alkaline solution illumination or presence of H acceptor suffices. In strongly alkaline solution, CO is oxidised to CO_2 in the dark in absence of H acceptor. If photosensitizer (e.g. adrenaline) is present, illumination by diffuse daylight is adequate. The reaction proceeds almost as rapidly at 5° as at 30° . It is not affected by CH_3O , HCO_2H , Fe^{II} , Fe^{III} , Cu, or Cu^{II} . The results must be borne in mind when the effect of CO on the respiration of cells is studied. W. McC.

Effect of temperature on the photographic process. II. J. Eggert and F. G. Kleinschrod (*Z. physikal. Chem.*, 1941, **A**, 189, 1—9).—The blackening produced on photographic plates by X-rays at temp. between 14° and -173° has been investigated. There is a general decrease in sensitivity as temp. is decreased. The behaviour of some reversal effects (Villard effect, and solarisation) at temp. between 20° and -160° was examined. The Villard effect, which is marked at higher temp., gradually disappears as temp. is reduced. A. J. M.

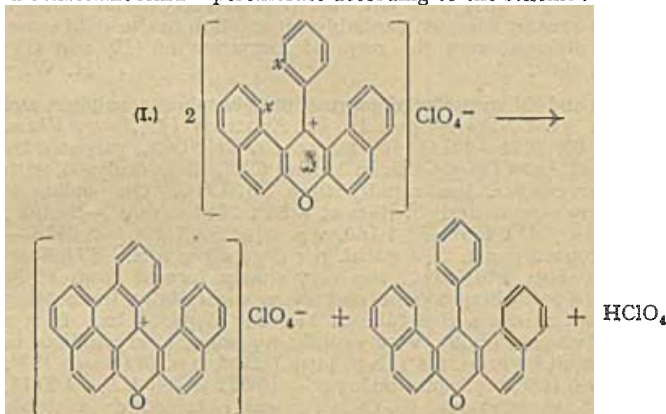
Photochemical nitration of benzene and nitrobenzene with nitrogen oxides. I. O. Gorislavetz (*J. Phys. Chem. Russ.*, 1943, **17**, 102—107).—Nitration of C_6H_6 vapour by NO_2 at $20-60^\circ$ is only slightly accelerated by illumination; visible light raises mainly the yield of $PhNO_2$, and ultra-violet light that of $C_6H_4(NO_2)_2$ etc. $PhNO$, vapour yields with NO_2 in light a mixture of $C_6H_4(NO_2)_2$ and $C_6H_3(NO_2)_3$. J. J. B.

Photo-oxidation in rigid media. G. N. Lewis and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1943, **65**, 2424—2426).—The role of electron-ejection in photochemical processes is discussed by reference to the odd-electron ions and radicals produced on illuminating org. substances, e.g., diarylamines, derivatives of Ph_2 and of C_6H_5 , in rigid media. W. R. A.

Photochemical reactions of leuco-dyes in rigid solvents. Quantum efficiency of photo-oxidation. G. N. Lewis and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1943, **65**, 2419—2423).—Absorption spectra of oxazine (I), thiazine (II), leuco-methylene-blue (III), leucothionine (IV), and Michler's hydride (V) in an EtOH-iso- C_6H_{12} - Et_2O mixture G (A., 1).

at liquid air temp. have been determined. (I) and (II) give, on illumination, two semiquinone forms, one by ejection of an electron and the other by loss of H^+ from the first on keeping. (III), (IV), and leuco-Capri-blue give, on illumination, five different substances, two of which are semiquinones, one is the completely oxidised dye ion, and the others are derived from the dimeric form of the leuco-base. Leuco-crystal-violet, leuco-malachite-green, and (V) behave similarly. Quantum yield of Wurster's-blue ions in the photo-oxidation of leuco-Wurster's-blue is 0.10 at the commencement of illumination. With (III), the quantum yield increases with concn. of leuco-base and decreases with increasing illumination; in conc. solutions the initial yield is 0.04. This behaviour demonstrates the existence of a dimeric leuco-base responsible for most of the oxidation products. W. R. A.

Mechanism of a photo-disproportionation reaction. E. Hertel and G. Sock (*Z. physikal. Chem.*, 1941, **A**, 189, 95—108; cf. A., 1936, 1120).—The photochemical disproportionation of 13-phenyl-dibenzoxanthanium perchlorate according to the scheme:



has been investigated. The reaction is truly photochemical with a quantum yield of 0.03—0.05. This is independent of intensity and frequency of the incident light, and of the concns. of starting materials and products, and of the presence of foreign substances (N_2 , H_2 , O_2 , *p*-benzoquinone). The extent of reaction is \propto quantity of light absorbed. Temp. coeff. is 1.1 for 10° . Since the quantum yield is independent of intensity only 1 mol. requires to be activated for reaction to occur. The reaction is intramol., consisting of a dehydrogenation leading to ring-closure at the positions marked x in (I), or to an initial step in this ring-closure. A. J. M.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Theory of isotope separation by exchange reactions. L. Waldmann (*Naturwiss.*, 1943, **31**, 205—206).—Mathematical. The application of the law of mass action to Urey's method of separating isotopes (A., 1939, I, 211) is considered in two limiting cases: (1) when the gas mols. dissolve unchanged in the liquid, (2) when there is extensive ionisation in the liquid. The general rule is obtained that in the equilibrium, gas \rightarrow dissolved mols. and ions, the heavier isotope is always enriched in the liquid if the ions have more internal degrees of freedom than the gas mols. Where there are fewer degrees of freedom of the ion, separation of the heavier isotope may occur in either phase. A. J. M.

Action of charcoal on potassium nitrate. II. T. M. Oza and M. Shah (*J. Indian Chem. Soc.*, 1943, **20**, 261—270; cf. A., 1943, I, 133).—A detailed study of the reactions between KNO_3 , KNO_2 , and C under different conditions, shows that the first reaction is $4KNO_3 + 3C = 4KNO_2 + 2CO_2$, and this may be followed by $4KNO_2 + 3C = 2K_2CO_3 + CO_2 + 2N_2$, proceeding smoothly to completion, or may become explosive when the reaction is $KNO_3 + KNO_2 + 2C = K_2CO_3 + CO_2 + N_2$. F. J. G.

More care with mercury.—See A., 1944, III, 362.

Chemical investigations of silicates. X. Topaz, $Al_2SiO_5(F,OH)_2$, and its synthesis; new aluminium oxide containing fluorine. R. Schober and E. Thilo (*Ber.*, 1940, **73**, [B], 1219—1240).—Comparison of the analytically determined F content of 3 topazes with the gitter vals. obtained by exposure of powders shows that there is no simple relationship between these magnitudes. Thermal hydrolysis of AlF_3 leads, according to the temp., to an *Al oxyfluoride* (I) of the approx. composition Al_2O_3F or to $\alpha-Al_2O_3$ (II). Up to 600° only (I) is produced, between 600° and 800° a mixture of (I) and (II) and $>800^\circ$ only (II). (I) has its proper lattice. The intensities of the lines in the Debye diagrams differ according as (II) has been prepared up to 550° or at $>600^\circ$. Very sharply defined limits of temp. are observed for the reaction, $2AlF_3 + 2SiO_2 = topaz$ (III) + SiF_4 . (III) is produced between 750° and 950° . Above and below these temp. there is

much loss of SiF_4 and a product (IV) results with a lattice closely resembling that of mullite. (IV) contains 5–6% F. The mechanism of formation of (III) through the gas phase of SiF_4 is shown by use of an excess of AlF_3 or SiO_2 to be: $4\text{AlF}_3 + 6\text{H}_2\text{O} = 2\text{Al}_2\text{O}_3 + 12\text{HF}$; $12\text{HF} + 3\text{SiO}_2 = 3\text{SiF}_4 + 6\text{H}_2\text{O}$; $2\text{Al}_2\text{O}_3 + \text{SiF}_4 + \text{SiO}_2 = 2\text{Al}_2\text{SiO}_5\text{F}_2$, or, summarising, $4\text{AlF}_3 + 4\text{SiO}_2 = 2\text{Al}_2\text{SiO}_5\text{F}_2 + 2\text{SiF}_4$. The sharp limits of temp. are ascribed to the need by SiF_4 of a definite energy of activation. The same limits of temp. are imposed for the production of (III) from SiF_4 and Al_2O_3 or from a mixture of $2\text{Al}_2\text{O}_3 + 1\text{SiO}_2$. Under defined conditions it is possible to prepare topazes with enlarged lattice, the phenomenon appearing parallel with the inclusion of Al_2O_3 , which must be in a particularly active form. Lattice enlargement follows when (III) is formed in presence of an excess of AlF_3 , which yields this active Al_2O_3 by hydrolysis or reaction with SiO_2 or when $\gamma\text{-Al}_2\text{O}_3$ is treated with SiF_4 at $700\text{--}800^\circ$; at this temp. (III) is not obtainable from $\alpha\text{-Al}_2\text{O}_3$. A substance resembling (IV) is not obtained by the reaction of SiF_4 with $\text{Al}_2\text{O}_3 + \text{SiO}_2$ at temp. not exceeding 1050° . Formation of (IV) from $\text{AlF}_3 + \text{SiO}_2$ does not, like that of (III), occur through SiF_4 but in another manner, probably by reaction in the solid state. The great differences in the rates of formation of (II) and (IV) favour this view. H. W.

Cyanates and thiocyanates of germanium, phosphorus, sulphur, and chromium. G. S. Forbes and H. H. Anderson (*J. Amer. Chem. Soc.*, 1943, 65, 2271–2274).—*Ge isocyanate*, $\text{Ge}(\text{NCO})_4$, prepared by the action of AgNCO on GeCl_4 in boiling C_6H_6 , is hydrolysed, with strong effervescence, less rapidly than $\text{Si}(\text{NCO})_4$. On cooling it becomes very viscous and solidifies at -65° . It has m.p. $-8\pm 0.5^\circ$, b.p. $204\pm 0.4^\circ$, $n_D^{25} 1.4858$, $n_D^{25} 1.760$, v.p. equation $\log p = 8.6578 - 2757/T$, Trouton const. 26.4 g.-cal. per degree per mol. *Thiophosphoryl isocyanate*, $\text{P}(\text{S}(\text{NCO}))_3$, was very slowly formed from PSCl_3 and AgNCO in boiling xylene and more successfully by heating $\text{P}(\text{NCO})_3$ and S in a sealed tube at 140° for about 12 hr. It is a colourless, viscous liquid, very rapidly hydrolysed, crystallises in long needles at 0° (m.p. 8.8°), b.p. (atm.) 215° , b.p. (30 mm.) 135° , b.p. (60 mm.) 150° , v.p. equation $\log p = 10.032 - 3492/T$, $n_D^{25} 1.5116$, $\rho 1.538$. *S monocyanate*, $[\text{S}_2(\text{OCN})_2]_n$, was obtained as a stable yellow solid by heating AgNCO and S_2Cl_2 in C_6H_6 ; the C_6H_6 solutions deposited also a brownish-yellow solid, unstable in air, and presumably *thionyl cyanate*, $[\text{SO}(\text{OCN})_2]_n$. *S monothiocyanate* was obtained as $\text{S}_2(\text{SCN})_2$ in solution but polymerised to an insol. red solid when S_2Cl_2 and AgSCN were boiled in C_6H_6 . Its chemical and physical properties are almost identical with those of thionyl thiocyanate $[\text{SO}(\text{SCN})_2]_n$ and sulphuryl thiocyanate $[\text{SO}_2(\text{SCN})_2]_n$. *Chromyl isocyanate*, $\text{CrO}_2(\text{NCO})_2$, formed when AgNCO and CrO_2Cl_2 are refluxed in CCl_4 is stable in solution only. On evaporation under reduced pressure a brown solid is obtained which explodes when dry. *Chromyl isothiocyanate*, $\text{CrO}_2(\text{NCS})_2$, may exist for a short time as a dark purple substance in CCl_4 at room temp. but decomposes explosively at higher temp. The following have been prepared (details not given): *Silicic acid* (b.p. $\sim 129^\circ$) and *POCl₃SCN* (b.p. $\sim 173^\circ$). W. R. A.

Preparation of pure heavy oxygen isotope and nitrogen ^{15}N . K. Clusius, G. Dickel, and E. Becker (*Naturwiss.*, 1943, 31, 210).—A separation tube consisting of six units with a total length of 82 m. was used. With the wire at 700° , the equilibrium $2^{16}\text{O}^{18}\text{O} \rightleftharpoons ^{16}\text{O}_2 + ^{18}\text{O}_2$ was set up, and $^{18}\text{O}_2$ separated at the heavy end, together with a little $^{17}\text{O}^{18}\text{O}$. This was further separated in another apparatus. $^{18}\text{O}_2$ has mol. wt. 35.99. N_2 containing 4% of $^{15}\text{N}^{16}\text{N}$, obtained from NH_4Cl containing an enrichment of ^{15}N , was separated. In the case of N_2 , the equilibrium $2^{14}\text{N}^{15}\text{N} \rightleftharpoons ^{14}\text{N}_2 + ^{15}\text{N}_2$ is not set up at the Pt wire. The mol. wt. of $^{14}\text{N}^{15}\text{N}$ separated was 29.015, the small difference between this and the theoretical val. (29.004) being ascribed to the presence of a small amount of $^{15}\text{N}_2$. The use of a suitable catalyst in the tube brings about the above equilibrium, and enables pure $^{15}\text{N}_2$ to be separated. A. J. M.

Application of the isotopic method to the investigation of the mechanism of chemical reactions. III. Mechanism of reaction of acid anhydrides with alcohols. IV. Reaction of xanthation, reaction of cellulose mercerisation, and structure of alkali-cellulose.—See A., 1944, II, 119, 122.

Recovery of elementary sulphur from gases containing hydrogen sulphide. J. K. Chowdhury and R. M. Datta (*J. Indian Chem. Soc.*, 1943, 20, 253–260).—Incorporation of Al_2O_3 or to a smaller extent of MnO_2 increases the efficiency of Fe_2O_3 as an absorbent for the recovery of S from gaseous mixtures containing H_2S . F. J. G.

Problems of systematic affinity theory. W. Biltz (*Z. physikal. Chem.*, 1941, A, 189, 10–37).—The affinity of S and P for metals is examined. There is a periodicity in the no. of sulphides and phosphides which a metal can form with position in the periodic table. Max. occur with the elements of group I which is due to the existence of stable poly-compounds, in which the valency of the metal is increased. Max. in groups IV and VIII are due to the

formation of sub-compounds. The stability of polysulphides increases on the left-hand side of the periodic system with increasing at. no. The stability of the sulphides agrees in general with the rule that of homologous elements of the principal groups and transition series the compounds of the lighter are less stable than those of the heavier elements. The types of linkage and lattice structure present in sulphides and phosphides are discussed, and the energy content of these compounds is considered. A. J. M.

Synthesis of ethylene complexes of platinum with four different substituent groups in the inner sphere. A. Gelman (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 310–313).—The geometrical isomerides $\text{C}_2\text{H}_4 \cdot \text{Pt} \begin{smallmatrix} \text{Cl} \\ \text{NH}_2 \end{smallmatrix} \text{Cl} \begin{smallmatrix} \text{Br} \\ \text{NH}_2 \end{smallmatrix} \text{Cl} \text{ (I)}$ and $\text{C}_2\text{H}_4 \cdot \text{Pt} \begin{smallmatrix} \text{Br} \\ \text{NH}_2 \end{smallmatrix} \text{Cl} \begin{smallmatrix} \text{Cl} \\ \text{NH}_2 \end{smallmatrix} \text{Cl} \text{ (II)}$ have the following properties: (I), greenish-yellow prismatic crystals, $n_D^{25} > 1.783$, $n_D^{25} 1.758$, insol. in cold HCl , decomposed by cold AgNO_3 ; (II), yellow crystals, $n_D^{25} 1.783$, $n_D^{25} 1.708$, sol. in cold HCl giving $\text{NH}_4[\text{Pt}(\text{C}_2\text{H}_4)\text{BrCl}_2]$, giving a very feeble opalescence with cold AgNO_3 . Attempts to obtain the anion $[\text{Pt}(\text{C}_2\text{H}_4)\text{ClBr}]^-$ led to displacement of C_2H_4 from the complex. L. J. J.

XI.—GEOCHEMISTRY.

Apparatus and methods for measuring the conductivity of natural waters in marine and semi-marine conditions. P. Ulyott and O. Ilgaz (*Rev. Fac. Sci. Istanbul*, 1943, 7, 190–227).—Conductivity data and composition of Black Sea and Mediterranean waters are recorded. (See also C., 1944, Part 2.) A. A. E.

Sediments of four woodland lakes, Villas Co., Wisconsin. I. W. H. Twenhofel, V. E. McKelvey, S. A. Carter, and H. Nelson (*Amer. J. Sci.*, 1944, 242, 19–44).—The sediments are described, and mechanical and chemical analyses given. L. S. T.

Age of the Universe and of three Spanish minerals. J. de D. L. Luna (*Inst. Geol. Min. España*, 1943, 11, 149–213).—A survey of methods for determining geological time. The age of the following minerals was studied by radioactive methods: pitchblende, from a middle carboniferous layer, (411), betafite from Cordoba (0.8), and torbenite from the granites of Colmenarejo (Madrid) (424×10^6 years). F. R. G.

Chromium minerals of Beni-Buscera (Gomara [Spanish Morocco]). A. de Gálvez-Cañero and J. de Lizaur y Roldán (*Inst. Geol. Min. España*, 1943, 11, 109–124).—Irregular deposits of chromite occur in association with serpentine, magnesite, and amorphous silicates. Cr does not occur in Spain. F. R. G.

Tantalites or niobates? A. de Larragán (*Inst. Geol. Min. España*, 1943, 11, 225–232).—Columbite (I) containing some Ta occurs in Galicia (Spain). Good quality (I) has a market val. similar to that of tantalite. F. R. G.

Structural type of perovskite.—See A., 1944, I, 79.

Spectrum analysis data on gypsum from Permian deposits of Tართ. L. M. Miropolski and S. A. Borovik (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 33–36).—Of the 55 elements sought spectrographically in 17 samples of gypsum only 15, viz., Li, Be, B, Mg, Al, Si, Ca, Ti, Mn, Fe, Cu, Sr, Y, Zr, and Bi, were found. There are no marked differences in composition of samples taken from different stratigraphical horizons. Secondary gypsum has a simpler composition than primary. Fe, Ti, and Cu appear to be responsible for colour. Mg, Si, Ca, Ti, Fe, and Sr are always present; Li, Be, Y, Zr, and Bi occur sporadically, and only as traces. L. S. T.

A monchikite from Takob (Tadjik Soviet Socialist Republic). S. D. Tschetverikov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 37–41).—An unusual occurrence of a dyke of black lamprophyric rock (monchikite) in a biotite granite is described. A chemical analysis [I. Tschin] is recorded. L. S. T.

Effect of salt admixtures on the dissociation of dolomite. L. G. Berg (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 38, 24–27).—The effect of mixing NaCl with dolomite (I) on the time-temp. curves of (I) is illustrated graphically and is discussed. L. S. T.

Oxidation by potassium hydrogen sulphate as a distinguishing feature between amphiboles and pyroxenes. M. R. A. Iyer (*Current Sci.*, 1943, 12, 271–272).—Data which show that in amphiboles the proportion of FeO oxidised to Fe_2O_3 by fusion with KHSO_4 is $>$ in pyroxenes of similar composition are tabulated. The extent to which oxidation takes place depends in some measure on the composition of the substance, e.g., a high % of MgO reduces the degree of oxidation. L. S. T.

Kaolin seams. J. R. O. de Villacián (*Inst. Geol. Min. España*, 1943, 11, 3–31).—Kaolin is considered to be formed from feldspar by H_2O at temp. $< 400^\circ$. More prolonged action or higher temp. produce cryst. kaolin. The formation of sericite from plagioclase occurs similarly with H_2O containing K^+ . F. R. G.

A I—General, Physical, and Inorganic Chemistry.

JUNE, 1944.

I.—SUB-ATOMICS.

Emissivity characteristics of hot metals, with special reference to the infra-red. D. J. Price and H. Lowery (*Iron and Steel Inst.*, March, 1944, *Advance copy*, 24 pp.).—The theoretical and practical considerations in connexion with the study of emissivity are discussed under the headings: definition of emissivity, basic theory, emissivity and pyrometer correction, experimental technique, and previous measurements. The relevant literature is critically surveyed, with 64 references. The application of emissivity data to correction of pyrometer readings is examined. Available information does not meet this need, especially in the case of Fe. Available data apparently indicate a zero temp. coeff. of emissivity for all substances at a sp. infra-red λ ; hence, at a certain λ for each substance the emissivity to a pyrometer would be much simplified.

T. D. F.

Determination of oscillation intensities in atomic spectra. D. S. Roshdestvenski and N. P. Penkin (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 97—101).—A graphite furnace in which metal vapours at 3000° can be examined is described. The anomalous dispersion of Fe vapours at 5060—5330 Å. could not be measured exactly because of the reaction between Fe and graphite; better results were achieved with the Cr triplet 5204.68—5208.59 Å. The probability of oscillations causing these lines agrees with theory. From the intensity of Na and Ba lines it is suspected that thermal equilibrium was not reached in the furnace.

J. J. B.

(A) Arc spectrum with carbon electrodes of cerium, neodymium, and praseodymium between 2200 and 5000 Å. for 2×10^{-4} , 2×10^{-5} , and 2×10^{-6} g. (B) Arc spectrum with carbon electrodes of dysprosium, holmium, and terbium between 2200 and 5000 Å. for 2×10^{-4} , 2×10^{-5} , and 2×10^{-6} g. J. M. López de Azcona (*Anal. Fis. Quím.*, 1940, 38, 154—164, 261—275; cf. A., 1940, I, 399).—(A) 202 lines are tabulated for Ce, persisting at a concn. of 2×10^{-4} , 130 at 2×10^{-5} , and 24 at 2×10^{-6} g. For Nd the figures are 249, 19, and 3, and for Pr, 179, 33, and 8 lines respectively. The most persistent lines are compared with those previously recorded.

(B) The corresponding figures for Dy are 194, 57, and 15, for Ho, 300, 107, and 38 (with 3 at 2×10^{-7} g.), and for Tb, 374, 154, and 15. The most persistent lines are compared with those previously recorded.

F. R. G.

Arc spectrum of tungsten. F. Poggio Mesorana (*Anal. Fis. Quím.*, 1942, 38, 281—295; cf. A., 1936, 916).—New levels in the arc spectrum of W together with those previously calc. are grouped into terms pertaining to the configurations $5d^46s$, $5d^46s$, $5d^46s6d$, $5d^46s6p$, and $5d^46p$.

F. R. G.

Relative energy distribution in the continuum of immersed sparks between 9000 and 5000 Å. H. Schubert (*Ann. Physik*, 1941, [v], 39, 295—307).—The intensity of spark discharges beneath the surface of H_2O and CCl_4 is investigated, the relative distribution being determined photographically and, under H_2O , photoelectrically. Within fairly wide limits of error the energy distribution is independent of the material of the electrodes and the nature of the liquid, but is not const. in the long- λ region. The half-val. width of the H α line is $100 \text{ Å.} \pm 10\%$.

A. J. M.

Absorption spectra of rare earths. A. N. Zaidel (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 111—113).—The spectrum of NdCl₃ in aq. HCl is not basically changed by heating the solution at 160° above the crit. temp., although the absorption bands (5800 and 5200 Å.) are shifted towards red by 20 Å. for every 100° temp. rise. It is suggested that the theory of spectrum line broadening by foreign gases may be extended to account for the widths of absorption bands of rare-earth ions in solution.

J. J. B.

True line breadth and oscillator strength of europium sulphate lines. G. Joos and K. H. Hellwege (*Ann. Physik*, 1941, [v], 39, 25—29).—Photometric data at 15° are compared with data at -190° for the Eu sulphate lines $^1F \rightarrow X_0$, 5793 Å., $^3F \rightarrow X_1$, 5257 Å., and $^1F \rightarrow X_2$, 4651 Å. Half-val. breadths in sec.⁻¹ at 15° are 4.35×10^{10} , 6.52×10^{10} , 9.72×10^{10} , respectively, and oscillator strengths added for the components of the lines are 1.4×10^{-10} , 9.7×10^{-9} , and 33.8×10^{-9} , respectively, $\sim 10^{-3}$ times < vals. for Pr sulphate.

L. I. I.

Influence of chemical binding on K X-ray absorption and emission spectra. I. B. Borovski (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 187—194).—The structure of the main edge of K absorption bands and its relation to interat. forces are discussed for various Ti, Mn, and V compounds.

J. J. B.

Compton effect diffusion of X-rays is less for an atom contained in a crystal than for the free atom. J. Laval (*Compt. rend.*, 1942, 215, 278—279).—Observed Compton scattering in diamond, Al, and sylvine crystals is < that calc. for corresponding free atoms.

N. M. B.

Possible explanation of the weakening of the Compton effect in crystals. J. Laval (*Compt. rend.*, 1942, 215, 359—360).—The weakening is attributed to the restriction of the Compton recoil electron to "allowed" energy bands.

N. M. B.

Photo-electric threshold of copper. A. Blanc-Lapierre (*Compt. rend.*, 1942, 215, 321—323).—Determinations on Cu foil, sealed in a vac. tube and exposed to Hg-arc radiation, give the val. 2660 Å. Vals. deduced from available curves for powdered or volatilised Cu are 2800 and 2650 Å., respectively.

N. M. B.

Determination of relatively short optical life-periods in an atomic jet. H. Bruck (*Compt. rend.*, 1942, 215, 431—433).—A small region of the jet is excited by electron impact, and the displacement from this region of the "centre of gravity" of the emission zone is determined. The theory of the method is outlined.

A. J. E. W.

Energy distribution among secondary electrons. I. Longitudinal magnetic field method. R. Kollath (*Ann. Physik*, 1941, [v], 39, 59—80).—In the magnetic analyser described, primary electrons from a hot filament in a narrow beam impinge on a target, and secondary electrons are constrained to follow a path, predetermined by diaphragms, into a measuring chamber, by the application of a variable longitudinal magnetic field, from the magnitude of which their energy is calc. Data are given for Ta, Mo, and Be targets. The method is applicable to photoelectrons.

L. J. J.

Effect of temperature on the secondary electron emission of metals. (A) R. Kollath. (B) A. Becker (*Ann. Physik*, 1941, [v], 39, 19—22, 23—24).—Comments on a paper by Reichelt (*ibid.*, 1940, [v], 38, 293).

L. J. J.

Diffusion of radiation in a gas discharge. F. A. Butaeva, L. M. Biberman, and V. A. Fabrikant (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 95—96).—Differences between diffusion phenomena involving particles and photons are discussed, and a method of taking photon diffusion into account in the theory of radiation from gas discharges is outlined.

J. J. B.

Electrical characteristics of the ozonator discharge.—See B., 1944, II, 93.

Position of the transuranic elements 93 and 94 in the natural system of the elements. C. Bedreag (*Compt. rend.*, 1942, 215, 537—539).—From a survey of available data, the elements are assigned to a new column between W, U, and Mn, Ma, Re.

N. M. B.

The ionisation method of measuring neutron energy. L. H. Gray (*Proc. Camb. Phil. Soc.*, 1944, 40, 72—101).—Using an ionisation chamber filled with a gas of the same at. composition as the walls, the energy E_n absorbed per unit vol. of the solid is the product of the ionisation J_n in the cavity, the average energy W used up in producing a pair of ions in the gas, and the stopping power ρ of the solid relative to the gas. Methods of estimating W and ρ are discussed, and it is concluded that at best the abs. determination of E_n is liable to errors of $\sim 5\%$.

H. J. W.

Absorption and coincidence experiments with ^{198}Au . N. Feather and J. Dainty (*Proc. Camb. Phil. Soc.*, 1944, 40, 57—71).—In addition to the radiations observed by other investigators, ^{198}Au emits a fairly intense γ -radiation of ~ 65 e.k.v. energy. This is distinguished from the K X-radiation of Hg, and it is not the K X-radiation of Pt. K-electron capture cannot take place in $> \sim 15\%$ of the disintegrations of ^{198}Au .

H. J. W.

Spectrum of β -rays from ^{131}I . N. A. Perfilov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 485—487).—Measurements by the cloud-chamber method indicate that the β -rays from ^{131}I , produced by bombardment of $\text{UO}_2(\text{NO}_3)_2$ with neutrons from $\text{Rn} + \text{Be}$, have a max. energy of ~ 1.07 m.e.v.

J. W. S.

Cosmic-ray showers containing non-synchronised particles. A. Freon (*Compt. rend.*, 1942, 215, 323—326).—Experiments with a special arrangement of counters indicate the presence of small showers arising from a meson which disintegrates above the apparatus, which receives a disintegration electron and one or several collision electrons. N. M. B.

Absorption of the hard component of cosmic radiation. M. E. Rose (*J. Franklin Inst.*, 1943, 236, 9—45).—Mathematical. A phenomenological theory of absorption of mesotrons in the atm. and in dense materials at and below sea-level is given. Assuming 2×10^{-6} sec. for the proper lifetime, the calc. energy distribution at sea level accords well with observations. The theory leads to satisfactory agreement between observed and calc. angular distribution at sea-level and absorption in Pb. N. M. B.

Angular distribution of shower particles. S. Z. Belenki (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 97—100).—A formula for the mean scattering angle of shower particles in passing through matter, taking ionisation losses into account, is derived. For the scattering in air, the mean angle is reduced from 18° to 12° by the ionisation losses for particles with 100 Me.v. energy, and from 60° to 27° for an energy of 30 Me.v. The theory only applies qualitatively for scattering by substances of high at. wt. H. J. W.

Photon in the quantum theory of radiation. J. Yvon (*Compt. rend.*, 1942, 215, 410—412).—Consideration of the transfer of an energy quantum from an excited to an absorbing atom leads to a representation of a photon as a complex potential vector. A. J. E. W.

Nature of the planets. A. Dauvillier (*Compt. rend.*, 1942, 215, 222—224).—The theory of planet formation from photospheric solar matter leads to the existence of large, low-density planets of light elements, and small dense planets nearer to the sun. This view of large planets is discussed in relation to their known structure to explain their density, colour, and spectral characteristics, and results are compared with observational data. N. M. B.

Incomplete separation of variables in calculations on poly-electron atoms. M. G. Veselov (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 102—106).—Mathematical. A method applicable to atoms with two valency electrons is developed and applied to Li^+ and Be^{++} . J. J. B.

New periodic table of the chemical elements. (A) J. Pinilla. (B) E. Selles (*Anal. Fis. Quím.*, 1940, 36, 227—228, 229—232).—(A) The table of Guzmán (A., 1940, I, 311) is criticised as not making a clear representation of the periodicity of the elements.

(B) Guzman's table is criticised on the grounds that the chemical properties of the elements cannot be expressed in precise mathematical terms. F. R. G.

Principle of spectral resolution in wave mechanics. J. L. Des-touches (*Compt. rend.*, 1942, 215, 523—525).—Mathematical. N. M. B.

Vortex atoms. F. H. Loring (*Chem. Products*, 1944, 7, 40).—The connexion between probability nos. (which enter into the at. nos. of the inert gases, and into special groupings of elements in the periodic table, as well as into a no. of properties of orbits in general) and Kelvin's theory of the vortex atom is discussed. A. J. M.

Evaluation of the cosmical number. (Sir) A. S. Eddington (*Proc. Camb. Phil. Soc.*, 1944, 40, 37—56).—The cosmical no., $N = \frac{4}{3} \times 2^{256} \times 136$, is a fundamental const., which enters into many physical formulae, and determines the ratio of the electrical to the gravitational forces between particles, the range and magnitude of the non-Coulombian forces between particles, and the cosmical repulsion manifested in the recession of the nebulae. Its interpretation as the no. ($\hbar k$) of protons and electrons in the universe is discussed at length. W. J.

II.—MOLECULAR STRUCTURE.

Band spectra and energies of dissociation of diatomic molecules. A. G. Gaydon. R. C. Pankhurst. R. F. Barrow. W. Jevons (*Proc. Physical Soc.*, 1944, 56, 204—212).—A discussion. Gaydon reviews spectroscopic methods of evaluating energies of dissociation (D), with special reference to CO , N_2 , and NO (see A., 1944, I, 95), and gives 9.764 e.v. as the most probable val. of D for N_2 . Pankhurst points out the uncertainties of evaluations of D due to long extrapolation of vibrational energy levels and to the arbitrary representation of potential energy as a function of internuclear distance. Barrow describes the trends of mol. consts. (electronic energies, vibrational frequencies, energies of dissociation, etc.) throughout the group of diat. oxides, sulphides, selenides, and tellurides of C, Si, Ge, Sn, and Pb. Jevons discusses the spectroscopic similarity between these group-IV—VI mols. and the group of mols. each of which consists of two group-V atoms, such as N_2 , PN , AsN , SbN , P_2 , As_2 , Sb_2 , and SbBi . W. J.

Presence of the Lyman band system of nitrogen in the ultra-violet radiation of the night sky. L. Herman (*Compt. rend.*, 1942, 215, 527—529).—Frequencies calc. by the Birge-Hopfield formula are

compared with experimental data for 83 bands of the N_2 system $\alpha^1\Pi_u \rightarrow \chi^1\Sigma_g$, and with vals. calc. by an alternative formula which is proposed, and leads to better agreement. N. M. B.

Emission band system of PbSe. R. F. Barrow and (Miss) E. E. Vago (*Proc. Physical Soc.*, 1944, 56, 76—78).—A band system ($\nu \rightarrow \chi$) of ~ 40 bands in the region 3350—3850 Å., excited by a heavy-current, uncondensed, positive-column discharge through PbSe in a SiO_2 tube, is photographed in dispersion ~ 7.4 Å. per mm. Vibrational analysis gives for the wave nos. of the band-heads the expression $\nu_{\text{head}} = 28,416.9 + (190.5u' - 0.6u'^2) - (277.4u'' - 0.56u''^2)$, where $u = v + \frac{1}{2}$. The identity of the val. of ω_0'' with that for the ground state of PbSe (cf. Walker *et al.*, A., 1938, I, 116) shows that the lower state of the new transition is the ground state. N. M. B.

Absorption spectrum of SnTe. R. F. Barrow and (Miss) E. E. Vago (*Proc. Physical Soc.*, 1944, 56, 78—85).—From absorption studies in the visible in the temp. range 800—1400°, data for ~ 140 bands are tabulated, and the bands are assigned to four systems, one of which has previously been observed in emission (cf. Barrow, A., 1940, I, 281). N. M. B.

Absorption spectrum of nitrogen dioxide on films of aromatic compounds. I. O. Gorislavetz (*J. Phys. Chem. Russ.*, 1943, 17, 97—101).—It was hoped to detect intermediate compounds by determining the absorption of films of C_6H_6 , C_{10}H_8 , anthracene, and PhOH in a NO_2 atm. Only a general absorption at $\lambda < 3680$ Å. (for C_6H_6) to < 5800 Å. (for PhOH) was observed. J. J. B.

Comparison of the spectra of nickel and cobalt halides in the crystalline and gaseous state. (Influence of the nature of the chemical bond on the spectra of uni- and bi-valent metal halides.) K. Butkowiak and I. Wojciechowska (*Z. physikal. Chem.*, 1941, B, 49, 131—144).—The absorption spectra of NiBr_2 , NiI_2 , and CoI_2 in the vapour state were determined in the range 7000—1900 Å. The absorption spectra of NiBr_2 and CoI_2 are obscured by those of Br_2 and I_2 , due to thermal dissociation. The spectrum of NiI_2 is so strongly obscured that it can be observed only by the addition of Ni. The observed max. are due to fission of unexcited halogen atoms from the mols. The absorption spectra of uni- and bi-valent metal halides in the cryst. and gaseous states are compared. At 140—150° a continuous max. at 2670 Å. was found in the absorption spectrum of saturated I_2 vapour; this does not appear in the band system of Pringsheim and Rosen (A., 1928, 1072). J. F. H.

Spectral investigation of high-frequency discharge in acetylene-air flame. V. S. Rossichin and V. P. Timkovski (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 219—221).—The combustion of a mixture of C_2H_2 25 and air 75% is accelerated by electric vibrations of frequency $> 3.4 \times 10^7$ cycles per sec. The emission spectrum of the flame in a field of 2.5×10^7 cycles contains, in addition to the usual bands, N₂ bands, more CN bands, and Zn lines (from brass electrodes). In a field of 3.7×10^7 cycles N_2 and N₂⁺ bands appear, and the intensity of CH bands (3900 Å.) and CN bands (3883 and 3871 Å.) rises; this is associated with the acceleration of combustion. J. J. B.

Relations between chemical activity and absorption in the ultra-violet of certain organic molecules. VII. Absorption spectra of the amides of acetoacetic acid. K. G. Naik, R. K. Trivedi, and B. N. Mankad (*J. Indian Chem. Soc.*, 1943, 20, 389—391; cf. A., 1944, II, 157).—Curves are plotted and discussed for aq. solutions of acetoacetanilide, -o- and -p-tolylamide, -m-4-xylylamide, -a- and -β-naphthylamide. N. M. B.

Absorption curve of periline. F. B. Shorland (*New Zealand J. Sci. Tech.*, 1943, 24, B, 159—160; cf. A., 1944, II, 113).—Absorption for the free base in CHCl_3 and the hydrochloride in 0.1N-HCl begins at 515 and 435 mμ. and exhibits max. at 470 and 398 mμ. and min. at 375 and 325 mμ. respectively. S. A. M.

Colour and constitution of azo-dyes.—See B., 1944, II, 102.

Absorption spectra of pyrethrum extracts.—See B., 1944, III, 76.

Pigments of cottonseed.—See A., 1944, III, 444.

Luminescence spectra of rare-earth ions. J. I. Larionov (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 107—110).—The discrete luminescence spectrum of Tb^{IV} in its salts and solutions is due not only to the presence of an unfilled 4f shell, but also to Tb^{IV} ion in salts and solutions being identical with the theoretical Tb^{IV} ion. The same identity holds for Cr^{IV} in a Cr_2O_3 phosphor and, perhaps, for Mn^{III} in a Mn-MgO.TiO_2 phosphor. The effect of the environment of the ion is discussed. J. J. B.

Luminescence spectra of electrolyte solutions. A. A. Schischlovski (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 126—129).—A review (cf. A., 1940, I, 66). J. J. B.

Spectral study of a luminescent reaction. P. Groh and A. Kirrmann (*Compt. rend.*, 1942, 215, 275—276).—The reaction $2\text{KOH} + \text{Cl}_2 + \text{H}_2\text{O}_2 \rightarrow 2\text{KCl} + \text{O}_2 + 2\text{H}_2\text{O}$ is accompanied by a red luminescence showing an unresolved band at ~ 610 — 650 mμ. with a max. at ~ 632 mμ., and a weaker, narrower band with a max. at ~ 578 mμ. Explanations are discussed. N. M. B.

Dielectric after-effect phenomena in phosphors. H. Ruffler (*Ann. Physik*, 1941, [v], 39, 203—208).—The after-effect in CdS-Cu phosphors, of varying [Cu] is investigated at different temp. (20—100°) in both the unexcited and the excited states. At const. temp. the after-effect diminishes with decreasing [Cu]. Exposure to light causes a considerable increase in the after-charge current, the increase being greater for lower than higher [Cu]. Increase of temp. accentuates the after-effect; in the case of unexcited phosphors this is independent of [Cu]. Irradiation increases the effect of temp. on the after-charge current considerably, and the higher is the [Cu] the greater is the increase. The results can be explained by assuming the presence of dipoles which determine both the dielectric and optical properties of the phosphor. A. J. M.

Characteristic frequencies. L. S. Mayantz (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 158—161).—Conditions are discussed for a definite frequency of the Raman spectrum to be a function of one linking only. The difference between the force consts. of similar mols., e.g., $(\text{CCl}_2)_2$ and $(\text{CBr}_2)_2$, cannot be immediately deduced from the shift of the characteristic frequency. J. J. B.

Calculation of the frequencies of polyatomic molecules. M. A. Eliashkevitch and B. I. Stepanov (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 155—157).—A method is indicated for calculating the vibration frequencies of polyat. mols. Application of the method to CH_4 , C_2H_6 , and C_3H_8 is successful. J. J. B.

Infra-red absorption spectrum of phosphorus trimethyl. F. J. Wagstaffe and H. W. Thompson (*Trans. Faraday Soc.*, 1944, 40, 41—42).—Measurements are recorded for the range 3—20 μ . F. L. U.

Infrared absorption spectra and structure of metallic carbonates, bicarbonates, and thiocarbonates. (Mme.) R. Duval, C. Duval, and J. Lecomte (*Compt. rend.*, 1942, 215, 526—526).—Approx. general data and their interpretation are given and discussed for 12 carbonates, 5 bicarbonates, and 5 thiocarbonates, all of unspecified metals. N. M. B.

Raman spectra of complex mercury halides.—See A., 1944, I, 85.

Raman spectra of liquid and solid chlorine, bromine, and iodine compounds of aluminium. H. Gerding and E. Smit (*Z. physikal. Chem.*, 1941, B, 50, 171—193).—Raman spectra of liquid and solid AlCl_3 have been examined at 215°, 180°, 170°, and 20°, AlBr_3 at 115° and room temp., and AlI_3 at 215° and room temp. For liquid AlCl_3 three polarised and four or five depolarised lines are found, agreeing with an Al_2Cl_6 mol. with D_{2h} symmetry. A model with tetrahedral distribution of Cl about two Al, the two tetrahedra having a common side, is postulated in preference to a planar distribution. This correlates the Raman lines found with nine Raman-active normal vibrations. AlBr_3 and AlI_3 give spectra agreeing with double mols. in both solid and liquid phases. AlCl_3 frequencies are lower for the solid than the liquid phase, whilst their intensities are unchanged. The 340 cm^{-1} line of the liquid appears as a double line in the solid. This decrease in $\Delta\nu$ is attributed to denser packing and consequent electrostatic interaction. No change is observed between 170° and 180°. L. J. I.

Raman spectra and structure of sulphuric acid. V. M. Kudrjavtzeva (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 131—143).—The ν of the Raman lines of H_2SO_4 at 0°, 35°, and 50°, and of aq. H_2SO_4 , Me_2SO_4 , and a mixture of H_2SO_4 and Me_2SO_4 (1:1) at 16° are determined; contrary to literature indications there are no lines between 2500 and 3000 cm^{-1} in pure H_2SO_4 . For the lines 382—1350 cm^{-1} in H_2SO_4 the probable vibrations in the mol. are suggested. The frequencies 160 and 275 cm^{-1} are attributed to H bonds between H_2SO_4 mols.; they persist in the H_2SO_4 - Me_2SO_4 mixture. The OH vibrations (3340—3650 cm^{-1}) of this mixture are similar to those in H_2SO_4 at higher temp. (60°), as both heating and dissolution destroy multimol. H_2SO_4 chains. J. J. B.

Ionisation, Raman spectrum and vibrations of perchloric acid.—See A., 1944, I, 127.

Raman spectra and structure of the orthophosphates, phosphites, and hypophosphites. J. P. Mathieu and J. Jacques (*Compt. rend.*, 1942, 215, 346—347).—Tabulated data on the frequencies, state of polarisation, and intensity of Raman lines for the Na and K salts lead to classifications of the corresponding modes of vibration and information on structure. N. M. B.

Depolarisation of the Raman lines of metamolybdic acid in aqueous solution. (Mlle.) M. Murgier and (Mlle.) M. Theodoresco (*Compt. rend.*, 1942, 215, 530—531).—A single polarised line, 950 cm^{-1} , has been obtained. The depolarised line is 853 cm^{-1} . Significance and interpretation are discussed. N. M. B.

Raman spectra of hydrocarbons. IV. $\beta\epsilon$ -Dimethyl- $\Delta^{\alpha\epsilon}$ -hexadiene and $\beta\epsilon$ -dimethyl- $\Delta^{\beta\delta}$ -hexadiene. F. F. Cleveland (*J. Chem. Physics*, 1944, 12, 53—55).—The olefinic lines of $(\text{CH}_2\text{CMeCH}_2)_2$ (I) and $(\text{CMe}_2\text{CH})_2$ (II) have the following Raman frequencies, relative intensities, and depolarisation factors: (I) 1297 (50), 1414 (430) 0.74, 1651 (1000) 0.21, 2977 (580) 0.28, 3074 (220) 0.78, (II) 1227 (75) 0.46, 1663 (1000) 0.18, 3012 (very weak), 3040 (very weak). Vals. for (I) agree with earlier data for CXY:CH , olefines, H 2 (A., I.)

and vals. for (II) show conjugation decreases in frequency of 19, 19, 0, 10 cm^{-1} relative to CXY:CHZ in dipentene. L. J. J.

Raman spectra of two forms of alloocimene. J. J. Hopfield, S. A. Hall, and L. A. Goldblatt (*J. Amer. Chem. Soc.*, 1944, 66, 115—118).—Two forms of alloocimene (I), A and B, have been isolated in the pyrolysis products of α -pinene at $\sim 375^\circ$, and, whilst both yield the same additive product with $(\text{CH}_3\text{CO})_2\text{O}$, they have different b.p., f.p., ρ , and Raman spectra. A exhibits a strong Raman displacement of 1365 cm^{-1} and B one of 1272 cm^{-1} , thus enabling identification of each in a mixture. The Raman spectra support the interpretation that A and B are two of the four possible geometrical stereoisomerides of (I). W. R. A.

Spectra of scattered light and viscosity of liquids. E. F. Gross and A. A. Siromiatnikov (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 144—147).—The intensity of light depolarised and scattered without frequency change is high in PhOH and *p*-cresol at 19°. At 140—174° this intensity is less, but a diffuse depolarised background appears on both sides of the unchanged frequency. The background is due to mol. movement and becomes noticeable when the relaxation time of a mol. is comparable with the period of light vibrations. J. J. B.

Relaxation and light scattering in liquids. M. A. Leontovitsch (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 148—149).—The λ distribution and degree of depolarisation in the Rayleigh line and its background are determined by application of the relaxation theory of viscosity. A connexion exists between double refraction in a flowing liquid, relaxation time, and depolarisation of scattered light. J. J. B.

Study of the structure of Rayleigh lines by means of resonance absorption. M. F. Vuks (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1941, 5, 150—154).—The light of a Na lamp is separated into a beam which passes through a wedge, and another which is scattered by liquid CCl_4 or C_6H_6 , and the scattered part of which passes through Na vapour. If the intensities of the beams are made equal by adjusting the wedge at room temp., a temp. increase of the Na vapour reduces the intensity of the second beam. This reduction is different for unscattered light, for light scattered by C_6H_6 , and for light scattered by CCl_4 ; this shows that the fine structure of the scattered line is not identical with that of the original line and depends on the scattering liquid. Similar results are obtained with a modification of the above method. The Na vapour temp. is changed between 100° and 350°. The results permit calculation of the intensity distribution in the Rayleigh line. J. J. B.

Production of a photo-voltage in phosphor cells. F. Goos (*Ann. Physik*, 1941, [v], 39, 281—294).—Phosphors with transparent, metal-sputtered electrodes behave like Se or Cu_2O photo-elements when exposed to light, giving a photo-e.m.f. In addition to a pure photo-effect there are disturbing secondary phenomena, including a crystal photo-effect. The effect is particularly marked with CdS-Cu phosphors, which are as good as Se. The effect is widely independent of phosphorescence properties. The photo-e.m.f. has been measured for CdS-Cu, CdS-Ni, and ZnS-Cu, and also for a non-luminous but photosensitive ZnS crystal, and for mixed phosphors ZnS-CdS-Cu. A rectifier action occurs at the boundary layer. Like Se, the max. in the spectrum of photo-e.m.f. in the case of CdS-Cu is displaced towards shorter λ . This is not so with the secondary current and dielectric const., which depend on the material of the base, and are connected with the phosphorescence. The e.m.f. is almost independent of temp. over the range —180° to 50°. The widening of the spectrum is due to secondary effects of the base. There is a change in the spectrum if the CdS-Cu cell is sputtered with Au instead of Pt. The spectral distribution is dependent on the conditions of prep. of the phosphor base and the nature of the photo-sensitive centres, but is independent of the luminescence. A. J. M.

Electrical conductivity of thorium oxide at high temperatures. M. Foëx (*Compt. rend.*, 1942, 215, 534—536).—Measurements on the compressed oxide in air, O_2 , N_2 , CO_2 , vac., H_2 , and CO in the range 600—2100° are given and discussed. The variation of resistance with temp. is more rapid than for most refractory oxides and its insulating power is inferior. The conductivity depends markedly on the nature of the gaseous medium. N. M. B.

Electrostatic contribution to hindered rotation in certain ions and dipolar ions in solution. III. T. L. Hill (*J. Chem. Physics*, 1944, 12, 56—61).—Effective dielectric consts. are calc. for glutamic acid and its ions, and an empirical relation between them valid for a no. of substances is indicated. (Cf. A., 1944, I, 78.) L. J. J.

Use of refractive index measurements in fatty acid ester analyses. K. F. Mattil and H. E. Longenecker (*Oil and Soap*, 1944, 21, 16—19).—The n (Abbé refractometer) of highly purified Me deoate, laurate, myristate, palmitate, and oleate and their mixtures have been determined at temp. from 20° to 45°. It is shown that for each ester the relation n_D/θ is linear and given by $n_D^\theta = x + a\theta$, where θ is the temp. $x = 1.4334, 1.4395, 1.4446, 1.4486$, or 1.4595 , and $a = -0.00040, -0.00039, -0.00039, -0.00039$, or -0.00038

for the respective esters, in the above order. The vals. 1.42515^{20.4°}; 1.43136^{20.4°}; 1.43667^{20.4°}; —; and 1.45157^{21.0°}, respectively, were determined by the more accurate Pulfrich refractometer. Me stearate had n_D^{20} 1.4365 and n_D^{25} 1.4345, Me linoleate n_D^{20} 1.4697, and Me linolenate 1.4692. Examination of binary mixtures of the esters at 30° and 45° showed that a linear relation exists between n_D and the % composition by wt. (but not with molar composition); a similar relationship holds for three- and four-component mixtures. (See also C., 1944, Part 3.) E. L.

Dispersion of magnetic birefringence. R. Servant (*Compt. rend.*, 1942, 215, 574—576).—The expression $C = c\lambda/(\lambda^2 - \lambda_0^2)$ for the Kerr const. C is applied to various substances, and its significance in the case of gases and liquids is discussed. N. M. B.

Hydrogen bond. L. Hunter (*Chem. and Ind.*, 1944, 155—157).—A review. The effect of the existence of the H bond in determining the properties of H₂O is discussed. Types of H bond involving the atoms F, O, N, and C are listed and discussed. A. J. M.

Hyperconjugation in paraffin hydrocarbons. G. W. Wheland and J. T. Pinkston, jun. (*J. Chem. Physics*, 1944, 12, 69).—Resonance energy due to hyperconjugation in paraffin hydrocarbons is shown to increase the energy of each C—C single bond without appreciably affecting its constancy from substance to substance. L. J. J.

Intermolecular correlation. A. Tschintschin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 482—484).—Mathematical. J. W. S.

Identity of the properties of covalencies and co-ordinations. J. P. Mathieu (*Compt. rend.*, 1942, 215, 325—327).—A review of various evidence shows that there are, at present, no experimental facts which establish, between covalencies and co-ordinations, a difference already abolished by electronic theory. N. M. B.

Connexion between decrease of refraction and reduction of susceptibility in crystal lattices and in molecules. T. Neugebauer (*Ann. Physik*, 1941, [v], 39, 241—260).—In the case of both decrease of refraction and reduction of susceptibility the wave equation of a double perturbation problem is involved, one perturbation arising from the field of the neighbouring ions, and the other from the field of the light wave or the external magnetic field. In the case of the decrease of refraction the second approximation of the characteristic function is used, whereas only the first is required for reduction of susceptibility. The quantum-mechanical basis of this is discussed. A simple method is described for the direct application of the formulæ deduced to multi-electron problems. The refraction of the HCl mol. is calc. with the aid of the new Hartree tables. A. J. M.

Symmetry of certain thermodynamic relations. J. W. Creely, G. C. Le Compte, and W. W. Lucase (*J. Franklin Inst.*, 1943, 235, 617—622).—The underlying similarity of thermodynamic relations between the variables which determine the state of a system, viz., heat content, intrinsic energy, work content, free energy, temp., pressure, entropy, vol. heat, and work, is emphasised. A. J. M.

Molecular structures of silicon dimethyl dichloride, silicon methyl trichloride, and trifluorosilicon chloride. R. L. Livingston and L. O. Brockway (*J. Amer. Chem. Soc.*, 1944, 66, 94—98).—From electron diffraction data for the vapours of SiMe₂Cl₂, SiMeCl₃, and SiF₃Cl the Si—C distances are < in SiMe₂, whilst the Si—Cl distances are approx. those in Si chlorides. The SiF₃ group in SiF₃Cl does not bind the Cl more tightly than in SiCl₄, in contrast to the behaviour of CF₃ in CF₃Cl. W. R. A.

Nature of static friction. W. Claypoole and D. B. Cook (*J. Franklin Inst.*, 1942, 233, 453—463).—From a brief crit. survey of factors concerned and the limitations of various approaches a more satisfactory view of the basic cause is developed in relation to modern experimental knowledge. N. M. B.

Molecular surface energy of sulphur dioxide additive compounds. III. J. J. Jasper and J. R. Bright (*J. Amer. Chem. Soc.*, 1944, 66, 105—106).—The influence of temp. on the mol. surface energy of the compound NPr₃SO₂ and the equimol. mixture of NPr₃ and SO₂ has been determined. Vals. of ρ , γ , and η are given for temp. between 0° and 45°. Eotvos consts. have been calc. and are < those for additive compounds of lower mol. wt., indicating that the temp. coeff. decreases with increasing mol. wt., whilst the tendency to associate increases. Parachor data suggest the presence of a N—O—S linking. W. R. A.

Parachor of chromium trioxide in water.—See A., 1944, I, 122.

III.—CRYSTAL STRUCTURE.

Improvements in practical Fourier analysis and their application to X-ray scattering from liquids. G. C. Danielson and C. Lanczos (*J. Franklin Inst.*, 1942, 233, 365—380, 435—452).—Mathematical. Results are applied to the X-ray analysis of molten LiCl. N. M. B.

Resetting a triclinic unit-cell in the conventional orientation. D. H. Donnay (*Amer. Min.*, 1943, 28, 507—511).—Procedure is escribed, and examples are given. L. S. T.

Ordered and disordered structures of titanates and ferrites and ordered transformations of the TiO₂ modifications. F. Brandan, E. Brandenberger, and P. Niggli (*Helv. Chim. Acta*, 1944, 27, 88—96).—Disordered forms of heteropolar substances such as Li₂TiO₃ and Li₂Fe₂O₄ are obtained by reactions in the solid state, quenching from the melt, or continuous tempering below the stability temp. of the disordered modification. Tempering of quenched Li₂Fe₂O₄ at 570° produces a tetragonal form in which the Fe and O are related as Ti and O in the ideal anatase structure. Li₂Ti₂O₆, obtained by reaction in the solid state and tempered for 40 hr. at 1200°, gives the same system of interference lines as Li₂TiO₃. ρ measurements show that some metal atom positions are empty. Li₂Fe₁₀O₁₈ gives an interference diagram similar to that of magnetite, for which a quarter of the positions occupied in FeO are empty. Magnetite has a regular distribution of Fe^{II} with co-ordination no. 4 referred to O, the AB₂ structure of the NaCl type thus being stabilised. When there are more O atoms than Fe, the latter structure is at first maintained, and then part of the Fe is transformed from an octahedral into a tetrahedral structure. Structures with unoccupied positions then permit entry of alkali metal atoms, as Li, which compensate electrostatically for the valency change, thereby stabilising the valency. Thus Li₂Fe₂O₄, ordered and disordered, possesses the FeO structure, and Li₂Fe₁₀O₁₈, the Fe₂O₃ structure, although in both cases the Fe is trivalent. The cell consts. of certain compounds containing Fe, Li, and O are given; they show the effect of replacement of Fe by Li to be small. Brookite, but not anatase, can be transformed into rutile. The flat (100) plane of brookite and the (100) plane of rutile remain parallel on transformation. Inside the flat plane the rutile needles lie in different directions, the c axes being either parallel to the c and b axes of brookite or in the directions of the zones (027) and (023) of brookite. J. O'M.-B.

Crystallography of acanthite, Ag₂S.—See A., 1944, I, 92.

Crystal structure of gillespite, BaFeSi₂O₁₀.—See A., 1944, I, 92.

Crystal structure of parkerite, Ni₂Bi₂S₂.—See A., 1944, I, 92.

Four known crystalline forms of soap. R. H. Ferguson (*Oil and Soap*, 1944, 21, 6—9).—A crit. survey. The existence of four cryst. polymorphic forms of pure Na soaps, viz., α , β (cf. Thiessen and Stauff, A., 1936, 1186), δ (cf. Ferguson *et al.*, A., 1943, 1, 306), and ω (probably identical with the " γ soap" of De Bretteville and McBain; A., 1943, I, 300), has been established by X-ray diffraction studies, the short (or side) spacing being especially valuable for phase identification. The cryst. phase composition of commercial soaps depends on the soap, moisture, and electrolyte composition of the system, and on the conditions of processing, e.g., rapid cooling of neat soap induces the formation of ω -soap, whilst slow cooling increases the amount of β ; working and extrusion of plastic soap also induce changes; thus extrusion of soap assists in producing phase equilibrium, and under appropriate conditions may induce change from β to ω , or the reverse. Each crystal form has its own field of stability, its composition, temp. range, and possible equilibria with other phases constituting the phase diagram for the particular soap-H₂O system involved. Whilst soap crystallising from solution in H₂O may form a crystal phase containing H₂O, it is very doubtful if this constitutes a definite hydrate; the X-ray diffraction patterns do not indicate any definite hydrates over the range 2.5—95% of H₂O, and the existing evidence suggests that the solid modifications of soap are of the nature of solid solutions, being cryst. phases of variable composition. It appears that no sol, gel, or mother-liquor exists in many types of bar soap, so that the old conception of commercial bar soaps as "fibres of insol. soap enmeshing a gel or sol of the more sol. soaps" must be modified. Also, in most commercial soaps, the "fractionation" of the fatty acids suggested by this old definition does not appear to occur, though a certain degree of fractionation between two different solid solutions may take place. E. L.

Variation of the magnetic anisotropy of stretched rubber as a function of tension. (Mme.) E. Cotton-Feytis (*Compt. rend.*, 1942, 215, 299—301).—On analogy with a uniaxial crystal, the anisotropy is measured by the Krishnan oscillation method as used for crystals. Data are tabulated and discussed. The anisotropy appears to increase to a max. when the mol. chains are oriented parallel under the effect of stretching. The anisotropy-tension curve is similar to the curve of intensity variation of the diffraction spots with tension in X-ray diagrams. N. M. B.

Magnetostriction of iron in intense magnetic fields. O. Rüdiger and H. Schlechtweg (*Ann. Physik*, 1941, [v], 39, 1—18).—Change in length due to magnetostriction in the direction of the field is calc., especially its asymptotic behaviour in intense fields, for all field-crystal lattice orientations. Comparison with experimental data for single crystals and quasi-isotropic polycrystals shows that any departure from calc. results can be expected only at higher field strengths. L. J. J.

Colour and constitution of glasses.—See B., 1944, I, 136.

Deformation of solids. C. de Carbon (*Compt. rend.*, 1942, 215, 241—244).—Deformations which give rise to departures from

Hooke's law can be considered as the sum of two terms, one independent of, and the other increasing with, time. Theorems of these two terms are postulated and examined mathematically.

N. M. B.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Physical properties of butadiene and styrene.—Sec B., 1944, II, 120.

Mol. wt., gram-molecule, and Avogadro's number. W. E. Duncan (Phil. Mag., 1944, [vii], 35, 73—80).—Difficulties may arise in dimensional theory if the distinction between mol. wt. (a ratio) and g.-mol. (a mass) is overlooked. Temp., the gas const., mol. heats, and latent heats are discussed as examples.

H. J. W.

Elementary processes in magnetisation in the region of initial susceptibility. G. Thiessen (Ann. Physik, 1941, [v], 39, 30; cf. *ibid.*, 1940, [v], 38, 153).—A correction.

L. J. J.

Temperature-dependence of the magnetic susceptibility of europium sulphate. H. Fritsch (Ann. Physik, 1941, [v], 39, 31—32).—Vals. for the magnetic susceptibility of Eu^{III} sulphate at 20°, 80°, 196°, and 356° K. are 1.29, 1.29, 1.16, and 0.83 times the val. at 0°.

L. J. J.

Gray and Cruickshank's method and the diamagnetic susceptibilities of dicyanodiamide, acetamide, and cyanuric acid. S. K. Siddhanta and P. Ray (J. Indian Chem. Soc., 1943, 20, 359—364).—Measurements on carefully purified specimens give results showing only moderate agreement with vals. calc. by Gray and Cruickshank (A., 1936, 19) from magnetic analysis of resonating mol. structures, but the latter are a marked improvement on vals. from Pascal's earlier procedure.

N. M. B.

Absorption of sound in mixtures of monatomic gases. M. Kohler (Ann. Physik, 1941, [v], 39, 209—225).—The effect of ordinary and thermal diffusion on the absorption of sound in mixtures of monatomic gases is investigated using the Enskog equations; the equations of motion are derived from the kinetic theory, and the propagation of waves of infinitely small amplitude is considered. A sound wave in the mixture produces periodic variations not only of ρ and temp., but also of the mean mol. wt. The equations of motion reduce to three linear homogeneous equations for ρ , temp., and mean mol. wt. In addition to the Kirchhoff terms arising from friction and thermal conduction, three new terms enter, due to diffusion; they depend on frequency and pressure. The first of these terms is due to the effect of ordinary diffusion, and is \propto diffusion coeff., to $(M_2 - M_1)/M_2$ (M —mol. wt.), to C_p/C_v , and to C_1/C_2 , the product of the mol. consns. The second term is due to thermal diffusion and is $\propto (C_p/C_v) - 1$, to C_1/C_2 , to $(M_2 - M_1)/M_2$, and to a coeff. which accounts for the thermal diffusion. The third term is due to increased thermal conductivity due to thermal diffusion. The possibility of deriving thermal diffusion coeffs. from determinations of sound absorption in gaseous mixtures is mentioned.

A. J. M.

Absorption of sound, specific heat, and period of adjustment of electron spin in nitric oxide. H. O. Kneser (Ann. Physik, 1941, [v], 39, 261—272).—The half-val. widths and frequencies of the resonance points of a cylindrical resonator are measured in NO by means of a condenser-microphone; the absorption and velocity (relative to air) of sound in the gas are obtained. Between 300 and 3000 cycles per sec. the absorption is too weak to be measured. The sp. heat is calc. from the velocity of sound, the val. obtained agreeing closely with that calc. from spectroscopic data. At these frequencies there is no delay in establishing thermal equilibrium, and the distribution of the mols. on the two levels of the split ground state occurs in $<10^{-8}$ sec. The probability of reversal of the electron spin in a gas-kinetic collision at 289° K. is $<1:6500$.

A. J. M.

Heat capacity, heats of transition, fusion, and vaporisation, vapour pressure, and entropy of *aaa*-trifluoroethane. H. Russell, jun., D. R. V. Golding, and D. M. Yost (J. Amer. Chem. Soc., 1944, 66, 16—20).—Vals. of C_p for CMeF_3 are measured calorimetrically from 12° to 220° K. The following vals. are found: m.p. $161.82 \pm 0.04^\circ$ K.; heats of transition, fusion, and vaporisation ~ 71 , 1480 ± 75 , and 4582 ± 5 g.-cal.; v.p., $\log p = 48.37340 - 2015.675/T - 16.81950 \log T + 0.0133816T$; $S_{298.16} = 60.87 \pm 0.15$; $S_{224.40} = 62.48 \pm 0.10$ (calorimetric) and 63.95 ± 0.10 (spectroscopic) g.-cal. per degree per g.-mol. at 0.9330 atm. There is thus a barrier of 3450 ± 400 g.-cal. per g.-mol. hindering internal rotation of the mol.

W. R. A.

Molecular heat of organic vapours. I. Method of measurement and preliminary results. A. Eucken and B. Sarstedt (Z. physikal. Chem., 1941, B, 50, 143—170).—The flow method of Blackett *et al.* (A., 1930, 282) is employed, with improvements which increase its accuracy for the measurement of mol. heats of org. vapours to $\sim 1\%$ at 200° and $\sim 2\%$ at 300°. C_p for C_6H_6 shows the temp. variation predicted from Kohlrausch's normal vibrations. C_p vals. for CCl_4 are $>$ those calc. from Planck's formula by ~ 1 g.-cal. per g.-mol., as a result of vibrational anharmonicity. For C_6H_{12} — C_7H_{16} the mol. heats are 3.5 — 7.0 g.-cal. $>$ existing published vals.

at 180°, but $<$ vals. predicted from Pitzer's theory by ~ 1 g.-cal. for *n*-paraffins and ~ 2 g.-cal. for isoparaffins.

L. J. J.

Transition temperatures and heats of transition of alkali hydrosulphides and hydroselenides.—See A., 1944, I, 38.

Thermal expansion of titanium. P. Hidnert (J. Res. Nat. Bur. Stand., 1943, 30, 101—105).—The coeff. of linear expansion of Ti (97.2%) increases from $\sim 5 \times 10^{-6}$ per °C. at -150° to $\sim 12 \times 10^{-6}$ per °C. at 650° . The data on thermal expansion do not indicate the existence of polymorphic transformations of Ti between -190° and 700° .

A. J. M.

Table of thermodynamic properties of air. J. H. Keenan and J. Kaye (J. Appl. Mechanics, 1943, 10, A123—130).—Over the range of conditions for which $p v = RT$ satisfactorily represents the p - v - T relation, a table having a single argument, *i.e.*, temp., serves all the purposes given by vapour (steam, NH_3 , etc.) tables having two arguments. A table of this type with intervals small enough for linear interpolation is presented for dry air. Data from the table are compared with the vals. of Gerhart *et al.* (A., 1942, I, 262).

R. B. C.

A steady-state problem in heat conduction. A. N. Lowan (Phil. Mag., 1943, [vii], 34, 502—504).—Mathematical.

W. J.

Problem in heat conduction. C. J. Tranter (Phil. Mag., 1944, [vii], 35, 102—105).—The temp. variation in a semi-infinite annulus bounded by the plane $z = 0$ and the cylinders $r = a$ and $r = b$, the surfaces $z = 0$ and $r = a$ being maintained at zero temp. and $r = b$ at $f(z)$, is solved in the case where the initial temp. of the annulus is zero (cf. Lowan, preceding abstract, for a steady-temp. solution).

H. J. W.

Viscosity of sulphuric acid.—See B., 1944, I, 133.

Viscosities of unsaturated six-membered isocyclic compounds. J. N. Friend and W. D. Hargreaves (Phil. Mag., 1944, [vii], 35, 136—142).—In the series C_6H_{12} , C_6H_{10} , C_6H_8 , the η decreases as the degree of unsaturation increases, but rises again in C_6H_8 . The rheochor (R) of the Ph group attached to alkyl groups is 100.7 (mean), but if the attached group is electronegative R is raised by up to 4.5 units above this. R increases with the mass of the substituent group in the Ph ethers.

H. J. W.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Viscosity of sulphuric acid [solutions].—See B., 1944, I, 133.

Chemical and biological studies of aqueous solutions of boric acid and of calcium, sodium, and potassium metaborates.—See A., 1944, III, 378.

Nucleus formation in aqueous solutions. U. Dehlinger and E. Wertz (Ann. Physik, 1941, [v], 39, 226—240).—The spontaneous formation of nuclei in supersaturated solutions of $\text{KAl}(\text{SO}_4)_2$ has been investigated at 0°, 20°, and 40°, by determining the time at which crystallisation begins. Below a concn. ~ 4 mol.-%, which is to some extent dependent on temp., no spontaneous nucleus formation sets in after a year. There is a sharp boundary between metastable and stable supersaturated solutions. An attempt to apply the theory of Volmer *et al.* on the formation of nuclei from the vapour state to this boundary curve shows that the sharpness of the experimental boundary and the effect of temp. on it do not agree with the theory. Nucleus formation by negative diffusion, however, gives a satisfactory explanation. It is assumed that each dissolved ion tends to surround itself with 6 H_2O mols. Thus above 4 mol.-% only a part of the ions is separated by a layer of H_2O mols. The Coulomb forces between the ions produce at lower temp. a max. in the variation of thermodynamic potential with concn. at ~ 4 mol.-% and thus a negative diffusion coeff. above this concn.

A. J. M.

Parachor of chromium trioxide in water. P. M. Toshniwal, V. A. Moghe, and W. V. Bhagwat (J. Indian Chem. Soc., 1943, 20, 341—342).—The parachor of CrO_3 (~ 103) indicates that in solution it exists in ionic form and by combining with H_2O forms H_2CrO_4 or $\text{H}_2\text{Cr}_2\text{O}_7$. The calc. val. is 134 and the difference suggests that ionic parachors are $<$ at. parachors for the same element.

C. R. H.

Pyrazine-water azeotrope. H. F. Pfann (J. Amer. Chem. Soc., 1944, 66, 155).—The azeotrope distils at 95.5° (uncorr.)/760 mm. and has $n_D^{25} 1.4510$, $d_4^{25} 1.06$, 60% pyrazine—40% H_2O . No azeotrope is formed with MeOH or EtOH .

W. R. A.

Iron-rich iron-nickel alloys.—See B., 1944, I, 171.

Solubilities of normal aliphatic nitriles of high mol. wt. C. W. Hoerr, E. F. Binkerd, W. O. Pool, and A. W. Ralston (J. Org. Chem., 1944, 9, 68—80).—The solubilities of deca-, dodeco- (I), myristo-, palmito-, and stearo-nitrile have been determined in C_6H_6 , cyclohexane (II), CCl_4 , CHCl_3 , Et_2O , AcOH , EtOAc , BuOAc , COMe_2 , COMeEt , MeOH , 95% EtOH , Pr^nOH , Bu^nOH , EtNO_2 , and MeCN . In general the solubilities decrease with increasing polarity of the solvent. In any given solvent, the solubilities decrease regularly as the mol. wt. of the nitrile increases. The aliphatic nitriles form simple eutectics with the non-polar solvents, C_6H_6 (II), and CCl_4 ;

the compositions and f.p. are recorded. Of the three non-polar solvents used the nitriles are most sol. in C_6H_6 and least sol. in CCl_4 . As the mols. are symmetrical and of practically identical dielectric const. it appears that the resonance of the C_6H_6 mol. is an important factor affecting the solubility of the nitriles. In general, the nitriles are less freely sol. in the slightly polar solvents, ($CHCl_3$, Et_2O , $AcOH$, $EtOAc$, $BuOAc$) than in the non-polar solvents but considerably more sol. in $CHCl_3$ than in CCl_4 at any given temp. They are less sol. in $COMe_2$ than in $COMeEt$; they are, however, more sol. in both of these solvents than in any of the less polar solvents except in the lower concn. ranges. They are less sol. in $MeOH$, 95% $EtOH$, $PrOH$, and $BrOH$ than in any of the preceding solvents. (II) is much less sol. in $BuOH$ than in $EtOAc$, the polarity of which is of the same order of magnitude as that of $BuOH$. The solubilities of the nitriles in the alcohols differ relatively little at corresponding temp. in spite of the wide range of polarity of the alcohols. The nitriles are less sol. in the highly polar $EtNO_2$ and $MeCN$ than in any of the other solvents investigated with the exception of the alcohols and less sol. in $MeCN$ than in $EtNO_2$. The shape of the solubility curves of the nitriles is characteristic of a wide variety of aliphatic compounds of high mol. wt. Mol. association is probably one of the factors influencing the slope of the temp.-concn. curve of long-chain compounds. No conclusions, however, regarding the nature or the extent of this association should be drawn until further investigations of the behaviour of long-chain compounds are available. H. W.

Solubilities of normal aliphatic primary amines of high mol. wt. A. W. Ralston, C. W. Hoerr, W. O. Pool, and H. J. Harwood (*J. Org. Chem.*, 1944, 9, 102—112).—The solubilities of decyl-, dodecyl-, tetradecyl-, hexadecyl-, and octadecyl-amine (I) have been observed in a no. of solvents. Their solubility graphs are similar to those of the fatty acids, ketones, and nitriles but they do not exhibit the marked correlation between solubility and polarity of the solvent which is so striking with the other compounds. They form simple eutectics with the non-polar solvents C_6H_6 , cyclohexane, and CCl_4 , the compositions and f.p. of which are determined. In these solvents they are most sol. in C_6H_6 and least in CCl_4 . Among the slightly polar solvents $CHCl_3$, Et_2O , $EtOAc$, and $BuOAc$ the highest solvent power is shown by $CHCl_3$. The solubilities in $EtOAc$ and $BuOAc$ are practically identical. The amines are somewhat more sol. in $COMeEt$ than in $COMe_2$. The solubility of (I) in $COMe_2$ becomes so limited that a considerable region consisting of two immiscible solutions appears. Of the fatty acid derivatives thus far investigated (I) is unique in forming conjugate solutions with a solvent of polarity as low as that of $COMe_2$. With $MeOH$, 95% $EtOH$, $PrOH$, and $BuOH$ the amines differ from other fatty acid derivatives in being more sol. in the lower members of the series than in any of the other solvents used except $CHCl_3$. The amines differ widely in their solubilities in the various alcohols whilst the solubilities of other long-chain compounds do not differ greatly in these solvents. In the highly polar $MeCN$ the amines are less sol. than in any other solvent studied and (I) shows a region of immiscibility similar to that found in the system, (I)— $COMe_2$. In this system the entire immiscible region exists below the b.p. of the solvent, and the upper limit of the region of conjugate solutions can, therefore, be located. The solubilities of the amines in $EtNO_2$ are not determinable owing to their reaction with this solvent. H. W.

Solutions of lead in its fused chloride. S. Karpatshev, A. Stromberg, and E. Jordan (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 101—104).—From measurements of the potential of a C electrode in a solution of Pb in fused $PbCl_2$ at 700° as a function of the concn. of the metal, it is concluded that the Pb goes into solution as a univalent positive ion. The solubility of Pb in $PbCl_2$ at 700° is 0.0417%.

Factors affecting precipitation of insoluble quinaldates. J. F. Flagg and F. T. McClure (*J. Amer. Chem. Soc.*, 1943, 65, 2346—2349).—Solubility products of insol. quinaldates have been found by a method involving fractional pptn. Applications of solubility data to problems of pptn. and separation with quinaldic acid are given. W. R. A.

Hysteresis and capillary theory of adsorption of vapours. L. H. Cohan (*J. Amer. Chem. Soc.*, 1944, 66, 98—105).—Several predictions based on the capillary theory of adsorption and the open pore theory of hysteresis show reasonable agreement with experimental data. This agreement indicates that the capillary theory, which postulates the formation of a unimol. layer followed by capillary condensation, is a fairly good first approximation for the adsorption mechanism in the systems discussed. Vals. of γ and mol. vol. of a liquid confined in a capillary of radius only twice the diameter of the liquid mol. appear to be approx. those for the liquid in bulk. W. R. A.

Water-adsorption isotherm of wool.—See B., 1944, II, 104.

Adsorption in relation to constitution. II. Adsorption of organic acids on activated silica gel. B. P. Gyani and P. B. Ganguly (*J. Indian Chem. Soc.*, 1943, 20, 331—337).—The adsorption on activated SiO_2 gel of a large no. of org. acids from $EtOH$ solution has been investigated. With the exception of $HCOEt$, adsorption of which

is high, the adsorption of fatty acids appears to be almost independent of chain length. The % adsorption of dibasic acids decreases with increase in the no. of C in the chain. The product of adsorption coeff. and the no. of C in the mol. is const. (~ 242) with the exception of $H_2C_2O_4$, for which the product is 167. This suggests that the mols. lie flat on the adsorbent surface. Substitution of OH and halogen increases adsorption, ($CHBr \cdot CO_2H$), being the one exception observed. Positional and optical isomerides differ little in adsorbability. C. R. H.

Adsorption of NN' -diethyl- ψ -isocyanine chloride on mica. T. Škerlak (*Kolloid-Z.*, 1941, 95, 265—286).—Polymerisation of NN' -diethyl- ψ -isocyanine chloride (I) is induced by adsorption on certain ionic lattices such as mica. Adsorption was examined by measurement of light absorption by the dyed mica plates. The difficulties in preparing satisfactory mica surfaces and in the light-intensity measurements are indicated. With increasing concn. of solutions of (I) the extinction rises rapidly to a max., indicating saturation of the surface. The amount of (I) adsorbed corresponds with a unimol. layer, the mols. being adsorbed on their long edge. Polymerisation occurs on adsorption as a consequence of this orientation. The distance between positively charged N atoms of (I) is approx. equal to that between points of negative charge in the cleavage surface of mica. Adsorption is reversible, and decreases with rising temp. The adsorption on Ag halides is of technical importance, and is in general similar, but is irreversible, indicating stronger forces. R. H. F.

Surface area of porous materials calculated from capillary radii. E. N. Harvey, jun. (*J. Amer. Chem. Soc.*, 1943, 65, 2343—2346).—Equations, based on the Kelvin formula, have been derived, by which the surface area of a porous adsorbent can be calc. from the high-pressure region of its adsorption isotherms. After correction for monolayer adsorption, and by using the desorption isotherm, surface areas are in good agreement with those obtained by the "point B" method. W. R. A.

Effect of electrolytes on the surface activity of solutions of paraffin chain salts. R. G. Aickin and R. C. Palmer (*Trans. Faraday Soc.*, 1944, 40, 116—120).—The treatment used by Cassie and Palmer (*A.*, 1941, I, 207) to calculate the change in potential energy in a surface film caused by increasing the concn. of counter-ions in the aq. solution is extended by taking into account the size of the ions. An expression is derived for the dependence of the lowering of interfacial tension on ion size, in satisfactory agreement with experimental data for the effects of Na^+ and K^+ on the tension of aq. Na alkyl sulphate-oil interfaces. F. L. U.

Minima in surface tension-concentration curves of solutions of sodium alcohol sulphates. G. D. Miles and L. Shedlovsky (*J. Physical Chem.*, 1944, 48, 57—62).—As dodecanol is added to solutions of Na dodecyl sulphate (I) the min. in the surface tension-concn. curves become more pronounced. The addition of a higher homologue of the corresponding sulphate to solutions of (I) or of Na tridecyl β -sulphate also causes pronounced min. Thus min. are due to the presence in the solution of more than one type of surface-active material; in the former case the presence of a slightly sol. surface-active substance and in the latter an admixture of two anionic surface-active electrolytes results in min. C. R. H.

Spreading of liquids on mercury surface. B. Ghosh (*J. Indian Chem. Soc.*, 1943, 20, 349—354).—For liquids to spread on Hg the presence of a promoter, the function of which is to spread a unimol. layer of some ion on the Hg, is necessary. For H_2O to spread, $\sim 10^{-8}$ g. of acid or salt per g. of H_2O is necessary. Alkaline salts are less effective. H_2O containing traces of colloidal Au or graphite spreads after irradiation with X-rays. For acid promoters $\sim 10^{14}$ H⁺ per 1 sq. cm. of Hg surface are necessary before spreading takes place. For the alkali halides the no. of cations necessary increases as the size of the cation increases. C. R. H.

Structure of an ovalbumin-detergent complex. K. J. Palmer (*J. Physical Chem.*, 1944, 48, 12—21).—A structure for a denatured ovalbumin-detergent (Nacconol NRSF) complex, which is in agreement with the results of Lundgren *et al.* (*cf. A.*, 1943, III, 838), consists of a polar protein monolayer with the detergent mols. adsorbed on one side only and with their long axes perpendicular to the protein layer. It is possible that the polar NH_2 -acids alternate along the peptide chain in ovalbumin. The structure of native ovalbumin is discussed and a schematic drawing, in which the mol. possesses one polar and two non-polar interfaces, is presented. With this structure it is possible to explain two facts with respect to native ovalbumin-detergent complexes, viz., the occurrence of free native ovalbumin in equilibrium with a complex containing 25% of detergent, and the presence in the complex of $<25\%$ of the detergent. C. R. H.

Theoretical considerations on emulsions and their separation. A. Dobrowsky (*Kolloid-Z.*, 1941, 95, 286—296).—The energy content of the emulsified phase is represented as a function of the degree of dispersiv. Applying the Boltzmann-Einstein statistical energy distribution theorem, the distribution of particle sizes is derived.

Assuming no disturbing factors, Stokes' law is applied to the falling particles, and a function obtained relating the vol. of the separated phase to the time. This is in satisfactory agreement with available data.

R. H. F.

Effect of sand on the viscosity, yield value, and thixotropic gelation of mud suspensions. J. N. Mukherjee and B. R. Majumdar (*Proc. Indian Assoc. Cult. Sci.*, 1943, 28, 3—4).— η and the cumulative vol. of H_2O of suspensions of Powai clay with two samples of sand, (i) 48—100- and (ii) >100-mesh, have been determined. With (i) there is no marked variation of η with sand concn., but addition of 5% of (ii) greatly increases η . Up to 3%, addition of both (i) and (ii) reduces the thixotropic gel strength, but above 3% it again increases. Relative yield vals. also vary with sand concn. The cumulative vol. of H_2O after 1 hr. increases up to 3% of sand, and then decreases.

W. R. A.

Bredig platinum sols. J. Mindel and C. V. King (*J. Amer. Chem. Soc.*, 1943, 65, 2112—2115).—Pt sols were prepared by arcing between 2-mm. Pt wires with d.c. of 220 v. and 4 amp., using H_2O , HCl (0.0001—0.0007N.), and HNO_3 (0.0001—0.0004N.) as dispersion media and air, O_2 , and N_2 as stirring gases. Composition and stability are only slightly affected by variation of dispersion medium and gaseous atm. The Pt content of the micelle is unaffected by coagulation with acids. Sols prepared by arcing in the gas phases are similar in all respects to normal Bredig sols. Formation of Bredig sols appears to follow the mechanism of formation of gas-phase sols which are stabilised by oxidation products of Pt formed when the Pt particles come in contact with H_2O .

W. R. A.

Osmotic activity of colloidal electrolytes. J. W. McBain and A. P. Brady (*J. Amer. Chem. Soc.*, 1943, 65, 2072—2077).—All osmotic coeffs. of colloidal electrolytes fall on three curves, one for straight-chain, one for branched, and one for polycyclic colloidal electrolytes and, consequently, activity coeffs. can be obtained with fair accuracy from one f.p. measurement. Both osmotic and conductivity data support the evidence of previous migration data that very dil. solutions contain a small proportion of highly conducting micelles. Addition of KCl or K_2SO_4 to very dil. solutions of K laurate promotes the formation of colloid and f.p. lowering is < additive, whereas at higher concns., where the colloid is already formed, the f.p. lowering is slightly > additive.

W. R. A.

Solubilisation and colloidal micelles in soap solution. J. W. McBain and K. E. Johnson (*J. Amer. Chem. Soc.*, 1944, 66, 9—13).—The solubilisation of H_2O -insol. dye by four K soaps has been measured for equilibrium conditions at various concns.; it increases so rapidly with the higher soaps as to suggest its incorporation between the lamellar micelles rather than dissolution in the hydrocarbon fraction of the micelle. KCl greatly increases the solubilising power of fully-formed micelles and produces micelles of still higher solubilising power in dil. solution.

W. R. A.

Comparative osmotic and viscosity measurements with polystyrene fractions. T. Alfrey, A. Bartovics, and H. Mark (*J. Amer. Chem. Soc.*, 1943, 65, 2319—2323).— η and π have been measured for PhMe solutions of polystyrene fractions, prepared by polymerising styrene at 60°, 120°, and 180° and fractionated by pptn. with MeOH from PhMe solution. The consts. k' and μ , of the viscosity and osmotic laws, and the mol. wt. have been calc. for each fraction. k' and μ differ for samples prepared at different temp.; the consts. of $[\eta] = KM^a$ also differ for different samples. It is suggested that, for fractions of equal mol. wt., case of pptn. is related to $[\eta]$.

W. R. A.

Dependence of viscosity on concentration in [solutions of] organic high polymers. M. Takei and H. Erbring (*Kolloid-Z.*, 1941, 95, 322—326).—The Philippoff-Hess eighth-power formula is modified by introduction of a term depending on particle shape. The modified formula is shown to reproduce the experimental data in three cases where the original formula failed, viz., "Cellite" in AcOH, polymerised ω -hydroxydecanoic acid in $(CHCl_3)_2$, and polystyrene in C_6H_6 .

R. H. F.

Analysis of thermodynamic measurements on highly elastic fibrous materials. E. Wöhlisch (*Kolloid-Z.*, 1941, 95, 296—302).—Highly elastic materials are characterised by their anomalous thermoelastic behaviour, which is described by a thermal extension coeff. and a thermal stress coeff. Materials are classified according to the magnitude of these coeffs., and data are given for some biological materials. Relations between measurable properties of stretched materials and thermodynamic magnitudes are indicated. Swelling and irreversible heat effects have in some cases to be taken into account.

R. H. F.

Molecular orientation and some properties determined by it in macro-molecular substances with chain and network structures. II. F. H. Müller (*Kolloid-Z.*, 1941, 95, 306—322; cf. A., 1944, I, 29).—The nature of the orientation distribution function is discussed for chain and network structures, and the change in directional distribution of bonds on deformation is examined. The return of stretched materials to the undeformed state requires time, which is shorter at higher temp. Below a certain temp. contraction no longer occurs and the material freezes up. The relaxation time,

which is obtained from the contraction-time curve, is related to the place-exchange frequency of monomer residues or small units. High viscosity and plasticity are consequences of low place-exchange frequency. It is necessary to assume a series of relaxation times in many cases. With polystyrene the relaxation spectrum shows two time groups, corresponding with movement of monomer residues and of whole mols. The variation of each with temp. accounts for freezing and flow phenomena.

R. H. F.

Statistical length of rubber molecules. L. R. G. Treloar (*Trans. Faraday Soc.*, 1944, 40, 109—116).—The length distribution for mols. containing up to 256 isoprene units is worked out by the methods previously used (A., 1943, I, 299) for paraffin chains.

F. L. U.

Isoelectric point of asclepin. D. C. Carpenter and F. E. Lovelace (*J. Amer. Chem. Soc.*, 1943, 65, 2364—2365).—Measurements have been made in the pH range 1.8—8.0 of the electrophoretic velocity of asclepin in citrate, acetate, and phosphate buffers. The electrical charge on the particle has been calc. The isoelectric point is at pH 3.11.

W. R. A.

Electrokinetics. XXVI. Electroviscous effect. III. β -Lactoglobulin systems. Interpretation of the meaning of $K\phi$ values obtained from electroviscosity data. D. R. Briggs and M. Hanig (*J. Physical Chem.*, 1944, 48, 1—12).—A modified form of the Krasny-Ergen electroviscosity equation, which gives better agreement with experimental data for colloid electrolytes, is proposed. The electroviscous properties of cryst. β -lactoglobulin (I) have been investigated at pH 6.60 and 4.22 with and without addition of NaCl. With increase of [NaCl] the entire change in η is due to a change in the extent of the electroviscosity effect. The degree of hydration, calc. vals. for which agree closely with those previously reported, is small, and little change occurs in its val. or in the asymmetry of the mols. as pH changes. It can be concluded that the mols. of (I) are rigid particles which are not subject to osmotic expansion or contraction when the nature or the no. of the gegenions is changed. Gum arabic is unlike (I) since it is subject to swelling and contraction under similar conditions. The system Na gum arabic—NaCl has been examined and compared with the (I)—NaCl system. The $K\phi/C$ vals. ($K = \text{const.}$ dependent on the shape of the micelle, $\phi = \text{viscometrically effective percentage vol. occupied by the colloid, } C = \text{concn.}$) for the former system decrease at high ionic strengths, whereas for the latter system the vals. are const.

C. R. H.

VI.—KINETIC THEORY. THERMODYNAMICS.

Equilibrium measurements by infra-red absorption for the formation of nitric acid from oxygen, water vapour, and nitrogen dioxide. E. J. Jones (*J. Amer. Chem. Soc.*, 1943, 65, 2274—2276).—By using the infra-red absorption at 1.4 μ of HNO_3 vapour a direct determination was made of the equilibrium const. for the reaction $H_2O(g) + NO_2(g) + \frac{1}{2}O_2(g) \rightarrow 2HNO_3(g)$ and the val. agrees with that of Forsyth *et al.* (A., 1942, I, 146). Transmission vals. of HNO_3 and HNO_2 in the 1.4 μ region are given.

W. R. A.

Microscopic equilibria in ampholytes. T. L. Hill (*J. Amer. Chem. Soc.*, 1943, 65, 2119—2121).—Mathematical. Microscopic and macroscopic equilibrium consts. are related by general expressions which have been derived. The concn. of a microscopic ion is given in terms of microscopic equilibrium const., $[H^+]$, and total concn. of ampholyte.

W. R. A.

Dissociation of dimethyl ether-boron trifluoride at low temperatures. H. C. Brown and R. M. Adams (*J. Amer. Chem. Soc.*, 1943, 65, 2253—2254).—Criticism of Laubengayer *et al.* (A., 1943, I, 193).

W. R. A.

Dielectric constant, ionic equilibrium, and ionic force in solutions. L. Ebert (*Naturwiss.*, 1943, 31, 263—265).—A review, dealing particularly with the work of Nernst.

A. J. M.

Basic ionisation constant of m -cresolsulphonaphthalein; pH values and salt effects. E. E. Sager, H. J. Keegan, and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1943, 31, 323—343).—The ionisation const. (K) of m -cresol-purple (I), calc. from spectrophotometric data for solutions of (I) in H_2O and HCl, is 1.98×10^{-2} , from which $pK = 1.703 \pm 0.005$. Activity coeffs. (f) of (I) determined in presence of KCl, $BaCl_2$, and $SrCl_2$ show that f passes through a min. at 0.2—0.5M-chloride, the f vals. being somewhat > vals. calc. from electro-metric data. The significance of this difference is discussed with reference to f vals. for the various ions involved.

C. R. H.

Lewis and Bronsted-Lowry definitions of acids and bases. I. M. Kolthoff (*J. Physical Chem.*, 1944, 48, 51—57).—The conflict between the two definitions is discussed. The term protoacids is proposed for acids conforming to the Lewis definition, whilst the Bronsted-Lowry definition should be left unchanged. The two concepts are complementary rather than contradictory.

C. R. H.

The Kirkwood-Westheimer theory of acid strength in the light of existing experimental data for dissociation constants of dibasic acids. W. F. K. Wynne-Jones and G. S. Rushbrooke (*Trans. Faraday Soc.*, 1944, 40, 99—109).—The Kirkwood-Westheimer theory (cf. A.,

1938, I, 574) is in only qual. agreement with data for the influence of solvent or temp. on the dissociation consts. of dibasic acids. Reasons are given for attributing the lack of better agreement to failure to take sufficient account of sp. interactions between solvent and solute mols. or ions. F. L. U.

Acid strengths of mono- and di-esters of phosphoric acid. *n*-Alkyl esters from methyl to butyl, the esters of biological importance, and the natural guanidinephosphoric acids. W. D. Kumler and J. J. Eiler (*J. Amer. Chem. Soc.*, 1943, 65, 2355—2361).—*K* of alkyl-phosphoric acids (alkyl = Me, Et, Pr^a, Bu^a, Me₂, Et₂, Pr₂^a, and Bu₂^a) have been measured. That the acid strengths of dialkyl > monoalkyl > unsubstituted H₃PO₄ is explained by solvation. Steric effects also exist and, to a smaller extent, statistical and inductive effects. Glycerol and sugar esters of H₃PO₄ are discussed with relation to these effects. The groups responsible for the dissociation of natural guanidinephosphoric acids have been assigned by analogy. Chelation through H-bonding and the inductive effect of the PO₄ group are discussed in relation to reactions of biological importance. W. R. A.

Ionisation of strong electrolytes. II. Ionisation, Raman spectrum, and vibrations of perchloric acid. O. Redlich, E. K. Holt, and J. Bigeleisen (*J. Amer. Chem. Soc.*, 1944, 66, 13—16).—A refined photographic method has been developed for comparing the intensities of spectral lines of unequal width. The degrees of ionisation of HClO₄ have been determined. It is ionised to a greater extent than HNO₃. The ionisation const. could not be calc. because the activity coeffs. are not known at high concns. Raman spectra of anhyd. HClO₄ and of conc. solutions of HClO₄ and NaClO₄ have been measured and are discussed. W. R. A.

pH values of certain phosphate-chloride mixtures, and the second dissociation constant of phosphoric acid from 0° to 60°. R. G. Bates and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1943, 30, 129—155).—The e.m.f. of cells of the type Pt|H₂|NaH₂PO₄ or KH₂PO₄ (*m*₁), Na₂HPO₄ (*m*₂), NaCl (*m*₃)|AgCl|Ag was determined at 5° intervals between 0° and 60°. Three vals. of *m*₁/*m*₂ were used, and a wide range of concn. was covered. The second dissociation const. (*K*₂) of H₃PO₄ was calc. The effect of temp. on $-\log K_2$ is given by $pK_2 = (1970.5/T) - 5.3541 + 0.019840T$, where *T* = abs. temp. For each temp. the heat and entropy of dissociation, the change of heat capacity and the free energy change accompanying the dissociation of 1 mol. of H₂PO₄⁻ were calc. The pH vals. of phosphate-chloride mixtures over the above temp. range are given by $(pH)_i = (pK_2)_i - \log (m_{H_2PO_4}/m_{HPO_4}) - 3A\sqrt{\mu}(1 + Ba_i/\mu)$, where μ = ionic strength, *a*_i is a parameter representing average ion size, and *A* and *B* are const. at a particular temp. This equation holds when $m_{H_2PO_4} = m_{Cl}$, and the ratio $m_{H_2PO_4}/m_{HPO_4}$ is 0.2—5.0. It is suggested that such solutions could be used as pH standards over the range 6.4—7.4. A. J. M.

pH values of acid-salt mixtures of some aromatic sulphonic acids at various temperatures and a criterion of completeness of dissociation. W. J. Hamer, G. D. Pinching, and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1943, 31, 291—304).—E.m.f. measurements show that aq. solutions of *p*-phenol- and 4-chlorophenol-2-sulphonic acids (>0.3*M*) are completely dissociated between 10° and 60°. The method used was to determine the activity coeff. (*f*) of HCl in the sulphonate solutions and to plot $-\log f$ against \sqrt{c} , where *c* = ionic strength. Since the vals. of $-\log f$ are > those predicted by Debye and Hückel's limiting law, it can be shown that the SO₃H groups must be completely dissociated. Solutions of the sulphonic acids, the corresponding Na or K sulphonates, and NaCl or KCl are suitable as pH standards over the pH range 1.2—2.5. C. R. H.

Complex ions. VIII. Pyridine-silver ions. W. C. Vosburgh and S. A. Cogswell (*J. Amer. Chem. Soc.*, 1943, 65, 2412—2413).—The results of the solubilities of AgIO₃, Ag₂SO₄, and AgBrO₃ in dil. C₅H₅N have been interpreted in terms of two complex ions, Ag⁺C₅H₅N⁺ and Ag(C₅H₅N)₂⁺, having dissociation consts. 1.0×10^{-2} and 7.8×10^{-8} . W. R. A.

Complex ions. VII. A solubility method for the determination of instability constants in solutions and the amines of nickel, cadmium, and magnesium. P. F. Derr and W. C. Vosburgh (*J. Amer. Chem. Soc.*, 1943, 65, 2408—2411).—The solubility of AgIO₃ in aq. NH₃ containing Ni, Cd, and Mg complexes of the form [M(NH₃)₆]²⁺ has been determined. The instability consts. of [Ni(NH₃)₆]²⁺, [Ni(NH₃)₅]²⁺, [Ni(NH₃)₄]²⁺, [Cd(NH₃)₆]²⁺, and [Mg(NH₃)₆]²⁺ have been calc. The solubility of Ba(IO₃)₂ and Ca(IO₃)₂ in aq. NH₃ has also been determined. W. R. A.

Thermodynamics of the nitrogen-hydrogen mixture. V. Fischer (*Ann. Physik*, 1941, [v], 39, 273—280).—A graphic method is described for the determination of the equilibrium concns. in a binary mixture when temp. and pressures occur which are above the crit. temp. and crit. pressure of the component of lower b.p. The method is used to calculate the equilibrium isotherms of a N₂-H₂ mixture. A. J. M.

System trimethyl phosphate-acetic acid. H. A. Pagel and W. V. Ruyle (*J. Amer. Chem. Soc.*, 1943, 65, 2186).—F.p. data for α-Me₃PO₄-AcOH mixtures give a eutectic at 52.9 mol.-% Me₃PO₄

with f.p. $-89.9 \pm 1^\circ$. F.p. of β-Me₃PO₄-AcOH mixtures could not be successfully determined at <75 mol.-% Me₃PO₄. W. R. A.

Systems with boron trifluoride. III. H. S. Booth and J. H. Walkup (*J. Amer. Chem. Soc.*, 1943, 65, 2334—2339).—Binary systems of BF₃ with the following F compounds have been investigated by thermal analysis: CF₂Cl₂, completely immiscible; CF₃Cl (m.p. $-181.6 \pm 0.5^\circ$) sol. in BF₃ up to 10 mol.-% and BF₃ sol. in CF₃Cl up to 20 mol.-% at -130.5° , whilst at higher temp. they are completely miscible; CF₄ (m.p. $-180.1 \pm 0.5^\circ$) sol. in BF₃ up to 15 mol.-% and BF₃ sol. in CF₄ up to 25 mol.-% at $-131.4 \pm 0.5^\circ$; PF₃ gives a eutectic at $-163.5 \pm 0.5^\circ$ and 21.5 mol.-% BF₃; POF₃ gives a eutectic at $-47.5 \pm 0.5^\circ$ and 16.5 mol.-% BF₃ and it is suggested that a 1:1 compound (f.p. $\sim -20^\circ$) is formed; PSF₃ (f.p. $-148.8 \pm 0.5^\circ$) gives a eutectic at $-152.1 \pm 0.5^\circ$ and 16.00 mol.-% BF₃, but the curve shows no max., although there is a change in slope at -130.8° and 82.5 mol.-% BF₃ probably owing to transition at this temp. of β-BF₃ to α-BF₃; SOF₂ (f.p. $-129.0 \pm 0.5^\circ$) forms a 1:1 compound (f.p. $-140.8 \pm 0.5^\circ$) and two eutectics at -145.9° (34 mol.-% BF₃) and -145.4° (68.5 mol.-% BF₃). W. R. A.

System Li₂SO₄-H₂O. A. N. Campbell (*J. Amer. Chem. Soc.*, 1943, 65, 2268—2271).—The following data are presented for the system Li₂SO₄-H₂O: (i) the transition point of the change Li₂SO₄·H₂O ⇌ Li₂SO₄ + H₂O, determined dilatometrically, thermometrically, and by v.p. measurements, lies at 232.8° and 26.7 atm.; (ii) the solubility between 110° and 214°; (iii) the ice line. The existence of a higher hydrate of Li₂SO₄, possibly Li₂SO₄·2H₂O, is considered to be doubtful, but is not entirely disproved by dilatometric methods or by a study of the equilibrium diagram of Li₂SO₄-LiCl-H₂O at -12.25° . W. R. A.

Reciprocal salt pair NaClO₃ + KCl ⇌ NaCl + KClO₃ in water at 0° and 40°. P. A. Munter and R. L. Brown (*J. Amer. Chem. Soc.*, 1943, 65, 2456—2457).—The isothermally invariant points for the system NaClO₃ + KCl ⇌ NaCl + KClO₃ in H₂O have been determined at 0° and 40°. The stable salt pair is KClO₃ + NaCl and appears to remain stable up to 100°. The isothermally invariant point of the system NaClO₃-KClO₃-H₂O at 0° is at 44.21:0.44-55.35%; those for NaClO₃-KClO₃-H₂O at 40° and for KClO₃-KCl-H₂O at 0° have been redetermined and agree closely with recorded vals. W. R. A.

Relations between daltonide and berthollide phases in metallic systems. N. V. Ageev and E. S. Makarov (*J. Gen. Chem. Russ.*, 1943, 13, 242—248).—The two phases are fundamentally of the same nature, and can pass continuously one into the other. Both owe their existence to formation of definite chemical compounds. R. T.

Dicalcium silicate solid solutions. K. T. Greene (*J. Res. Nat. Bur. Stand.*, 1944, 32, 1—10).—X-Ray diffraction, optical, and thermal data show that at $\sim 1450^\circ$ 2CaO·SiO₂ forms, with Na₂O and Al₂O₃ (or Fe₂O₃), solid solutions with hexagonal crystal structures, this structure being the fundamental one for α-2CaO·SiO₂ since it reverts to the β-form on cooling. When cooled below 1175° the material becomes inhomogeneous and Na₂O and Al₂O₃ (or Fe₂O₃) are thrown out of solid solution at the same time as the α-form is transformed into the β-form. The α-β inversion temp. lies within the range 1175—1420°, approaching the upper temp. as the purity of the 2CaO·SiO₂ becomes greater. The conditions of cooling Portland cement clinker are unfavourable to the preservation of the α-solid solution; to retain the α-form the % of Na₂O must be that normally present in commercial clinker. C. R. H.

Phase equilibrium in the system Li₂O-Al₂O₃-SiO₂. R. A. Hatch (*Amer. Min.*, 1943, 28, 471—496).—Liquidus and solidus temp. for preps. in the range 22—85% SiO₂ of the system Li₂O-Al₂O₃-SiO₂ are recorded, and represented graphically. Three-component compounds in the system are (i) β-spodumene (I), Li₂O·Al₂O₃·4SiO₂, a high-temp. form melting congruently at 1423°, and (ii) β-eucryptite (II), Li₂O·Al₂O₃·2SiO₂, melting, with dissociation, at 1397°. No compounds with the compositions of petalite (III), Li₂O·Al₂O₃·8SiO₂, or Li orthoclase are stable above the solidus. (III) dissociates at $>950^\circ$. The system includes (i) the SiO₂ field, (ii) the (I)-SiO₂ solid solution field, (iii) the field of (I) solid solution, (iv) the (II) solid solution field, (v) the γ-Al₂O₃ field, and possibly the Li aluminate field. Attempts to synthesise α-spodumene hydrothermally at pressures <100 atm. and at temp. from 400° to 500° failed; (I) always crystallised from the spodumene glass. Vals. of *n* for glasses in this system are given. L. S. T.

System CaSiO₃-CaAl₂Si₂O₈-NaAlSi₃O₈. W. K. Gummer (*J. Geol.*, 1943, 51, 503—530).—Thermal data obtained at high temp. and normal pressures are recorded. Phase equilibrium diagrams are reproduced, and the course of crystallisation in typical mixtures of the above compounds is discussed. L. S. T.

Systems lead oxide-alumina and lead oxide-alumina-silica. R. F. Geller and E. N. Bunting (*J. Res. Nat. Bur. Stand.*, 1943, 31, 255—270).—In the system PbO-Al₂O₃ evidence has been obtained for the existence of a compound PbO·Al₂O₃, unstable at $>970^\circ$ and forming a eutectic with PbO (94% PbO) of m.p. 865°. In the

system $\text{PbO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, the compounds $8\text{PbO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, $4\text{PbO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and $6\text{PbO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ have been identified, with incongruent m.p. 735° and 837° and congruent m.p. 811°, respectively. Evidence has also been obtained for the existence of four other compounds of undetermined composition. Al_2O_3 (purity >99.9%) has m.p. $2035 \pm 10^\circ$. J. W. S.

Thermodynamics of the reduction of magnesium oxide with carbon and calcium carbide. B. Mauderli, E. Moser, and W. D. Treadwell (*Helv. Chim. Acta*, 1944, 27, 105–116).—Reduction of MgO by C and CaC_2 is examined by calculations of the free energies of reduction from known thermal data. A distinctive feature of the method is the use of the entropy-log mol. wt. graph to calculate the entropy of CaC_2 . The reduction is easier with CaC_2 , but at low temp. a part is obtained as carbides, which dissociate to Mg and C again in the range 800–1000° (A., 1937, I, 320). In experiments on the thermal dissociation of CaC_2 in a vac. between 1800° and 1800° 94% of the C was recovered as graphite, and no C_2H_2 was found when the products were treated with H_2O . J. O'M.-B.

VII.—ELECTROCHEMISTRY.

Conductance of salts in ethylenediamine. W. H. Bromley, jun., and W. F. Luder (*J. Amer. Chem. Soc.*, 1944, 66, 107–109).—Conductances of KI, AgI, and AgNO_3 in $(\text{CH}_2\text{NH}_2)_2$ (9×10^{-2} mho) have been measured at 25° using concns. sufficiently low to permit calculation of Λ_0 and K . A suggested explanation for the very low val. of K for AgI is based on the electronic theory of acids and bases. W. R. A.

Mechanism of electrical conduction in the Nernst pencil. C. Wagner (*Naturwiss.*, 1943, 31, 265–268).—A review dealing particularly with electrolytic conduction of heated oxide filaments, the nature of the ions carrying the current, and the reasons for the higher conductivity of mixed oxides compared with single oxides. A. J. M.

Discussion and interpretation of the migration data of laurylsulphonic acid in aqueous solution. P. Van Rysselberghe (*J. Physical Chem.*, 1944, 48, 62–65).—Comparison of the author's calc. vals. for the transference no. of the laurylsulphonate radical with experimental vals. obtained by McBain (cf. A., 1943, I, 226) for solutions of laurylsulphonic acid indicates the probable presence of large amounts of nearly neutral micelles with compensating migrations at concns. above the max. in the transference curve, i.e., at acid concns. >0.055M. At concns. <0.055M, the agreement between calc. and observed vals. is excellent. Errors in one of McBain's data tables are corr. C. R. H.

Potentials of electrochemical phase systems. E. Lange (*Naturwiss.*, 1943, 31, 260–263).—A review. A. J. M.

Diffusion potential in solutions of electrolytes. J. J. Hermans (*Naturwiss.*, 1943, 31, 257–260).—A review, dealing particularly with the work of Nernst. A. J. M.

Geo-electric effect in membranes. L. Brauner (*Rev. Fac. Sci. Istanbul*, 1942, 7, 46–102).—From measurements using NH_3 and KCl solutions it is inferred that the change in potential across a membrane separating solutions of different concns. on bringing it from a vertical to a horizontal position (geo-electric effect of the first order ΔE) is due not to gravitational stratification of the diffusing solution, but to a direct influence of gravity on the relative mobilities of the ions. Investigations with various salts diffusing through a vertical parchment paper (anionic) membrane show that the rate of loss of p.d. is the more rapid the greater is the mobility of the cations and the more inert are the anions, whereas when the more conc. solution is above the membrane and the more dil. below it the reverse is the case. Both the membrane potential and the ΔE are reduced by a decrease in pH, and with protein (cationic) membranes ΔE changes in sign at pH vals. < the isoelectric potential. When two electrodes filled with the same solution (<10⁻²N.) are separated by a horizontal membrane an e.m.f. is established when the solutions are one above the other, the lower layer being positive with an anionic and negative with a cationic membrane. This effect ("geo-electric effect of the second order") is attributed to the shifting of the mobile part of an electrical double layer under the action of gravity. The adsorption potential, ionic mobilities, d of the ions, and the conductivity of the solution all affect its magnitude. From the results obtained it is inferred that the actual d of all ions in aq. media is >1. J. W. S.

Development of polarography. K. Bennewitz (*Naturwiss.*, 1943, 31, 268–270).—A review, tracing the development of polarography from Nernst. A. J. M.

Polarographic investigation of hydrogen bonding. II. Nitroresols. M. J. Astle and W. P. Cropper. III. Nitrodi-hydroxybenzenes. M. J. Astle and S. P. Stephenson (*J. Amer. Chem. Soc.*, 1943, 65, 2395–2399, 2399–2402; cf. A., 1943, I, 155).—II. The reduction at various pH of 3:1:2-, 4:1:2-, 5:1:2-, 4:1:3-, 6:1:3-, 2:1:4-, and 3:1:4- $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}$ at the dropping Hg cathode has been studied. Half-wave potentials are most negative when NO_2 is p and least negative when o to OH . p - NO_2

is reduced to NH_2 at all pH: o - NO_2 is reduced to $\text{NH} \cdot \text{OH}$ at pH <7 and to NH_2 at pH >7; m - NO_2 is reduced at pH <7 to $\text{NH} \cdot \text{OH}$ and NH_2 in two distinct steps, whilst at pH >7 reduction stops at $\text{NH} \cdot \text{OH}$. These results indicate a stabilisation of o - NO_2 by H-bonding, absent in p - NO_2 , and that reduction to NH_2 at pH >7 can occur only through the quinonoid form of the nitroresol.

III. The reduction at various pH of 2:1:3- (I), 4:1:3- (II), 3:1:2- (III), 4:1:2- (IV), and 2:1:3- $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OH})_2$ (V) has been studied with the dropping Hg cathode. When H-bonding is sterically possible [(I), (III), and (IV)] ease of reduction of NO_2 is > in (IV), where a H-bond is not possible. Similarity to (III) and (V) shows that (I) must have only one H-bond. A weak H-bond seems to exist in (II) at pH <5. At pH >9, (IV) is reduced in two separate steps to 4-nitroso- and 4-amino-pyrocatechol, but at pH <9, as for all the other compounds, direct reduction to NH_2 occurs. Introduction of a second OH weakens the H-bond between o - NO_2 and o -OH, and the ease of reduction of NO_2 depends on the relative position of the two OH. W. R. A.

Polarographic studies of sulphonamides. I. Oxidation products of sulphanilamides. N. I. Levitan, I. M. Kolthoff, W. G. Clark, and D. J. Tenenberg (*J. Amer. Chem. Soc.*, 1943, 65, 2265–2268).— p -Hydroxylamino- (I), 4:4'-azoxy-, and p -nitro-benzenesulphonamide have been investigated polarographically, and are capable of electrolytic reduction at the dropping Hg cathode. The mol. compound of 2 mols. of (I) and one mol. of sulphanilamide (II) has also been investigated polarographically. Bacteriostatic activity of (I) against *Escherichia coli* in vitro is that of (II). W. R. A.

Neutralisation reactions in selenium oxychloride. Potentiometric titration. W. S. Peterson, C. J. Heimerzheim, and G. B. L. Smith (*J. Amer. Chem. Soc.*, 1943, 65, 2403–2406).—Potentiometric titration for several acid-base reactions in SeOCl_2 has been investigated. The Müller "retarded electrode" has been adapted and a KCl reference electrode developed for the potentiometric titration of non-protonic neutralisations in SeOCl_2 . The relative strengths of the acids and bases have been determined, and are in the order $\text{SO}_3 > \text{FeCl}_3 > \text{SnCl}_4$; isoquinoline > quinoline > $\text{C}_6\text{H}_5\text{N} > \text{KCl}$. W. R. A.

Compounds of iron deposited on both poles simultaneously. G. Antonoff (*J. Physical Chem.*, 1944, 48, 21–23).— $\text{Fe}(\text{OH})_2$ (30 g.) was suspended in 2 l. of H_2O containing 2 c.c. of conc. H_2SO_4 and the suspension electrolysed at 60° with Pt electrodes (2×2 in.), keeping the liquid stirred; the current was ~2 amp. and the voltage varied over a wide range. If the cathode was inserted in a porous cup deposits were obtained which were similar to those obtained at the anode. The deposits appeared to be complex peroxides of Fe. X-Ray analysis did not offer any explanation of their composition or structure. C. R. H.

VIII.—REACTIONS.

Pyrolysis of digermane. H. J. Emeléus and H. H. G. Jellinek (*Trans. Faraday Soc.*, 1944, 40, 93–99).—The thermal decomp. of Ge_2H_6 in the range 195–220° resembles kinetically that of C_2H_6 and Si_2H_6 . It has an induction period, is of the first order and homogeneous in the middle stages, and is retarded later. The activation energy, 33.7 kg.-cal., is assumed to be associated with a disruption of the Ge-Ge bond. The data are discussed and a chain mechanism is proposed. F. L. U.

Kinetics of the decomposition of sodium hypochlorite. A. Rius Miró and J. M. González Barredo (*Anal. Fis. Quím.*, 1940, 38, 332–334).—A study of previous work on the decomp. of NaOCl leads to the conclusion that the reaction is autocatalytic. F. R. G.

Autoxidation of inorganic reducing agents. II. Stannous chloride (experimental). III. Stannous chloride (theoretical). S. J. Lachman and F. C. Tompkins (*Trans. Faraday Soc.*, 1944, 40, 130–136, 136–141).—II. Results are given for the rate of oxidation of aq. SnCl_2 at 30° by O_2 . The effect of varying the concn. of SnCl_2 , of added chlorides, and of various impurities was examined.

III. Analysis of the experimental curves indicates that the rate is $\propto [\text{HSnCl}_3]^{\frac{1}{2}}$. Other species may be oxidised much more slowly. The increase in the rate of oxidation caused by adding Fe salts is $> \propto [\text{Fe}^{+++}]$, in contrast to its effect on the oxidation of TiCl_3 (cf. A., 1943, I, 38). F. L. U.

Elimination of bromide ion from aqueous solutions of phenylbromoacetic acid. H. M. Dawson, W. R. Bulcraig, and G. F. Smith (*J.C.S.*, 1944, 90–94).—A general equation and three simpler equations valid under restricted conditions have been derived and satisfactorily applied to kinetic data for the elimination of Br^- from HNO_3 solutions of $\text{CHPhBr} \cdot \text{CO}_2\text{H}$ (I) in presence of NaNO_3 . The increase in reaction coeff. with increase in $[\text{HNO}_3]$ is due either to hydrolysis of (I) or to the primary salt effect of HNO_3 on the sp. reaction rate of the ion brought about by increase in $[\text{HNO}_3]$. The latter alternative is preferred and it is shown that the reactivity of undissociated (I) cannot be > 0.002 of that of $\text{CH}_2\text{PhBr} \cdot \text{CO}_2^-$. The dissociation const. of (I), calc. from kinetic data, is 6.1×10^{-5} at 25°. C. R. H.

Transformation of diazocyanides. M. A. Saboor (*Indian J. Physics*, 1943, 17, 223—228).—The rate of spontaneous transformation of *cis*- to *trans*-*p*-chlorobenzenediazocyanide in C_6H_6 and CCl_4 solutions has been followed by dielectric const. measurements. The half-life period is independent of initial concn., indicating a first-order reaction. Measurements of velocity coeffs. at various temp. give ΔE of activation of ~ 23 kg.-cal. W. R. A.

Inflammability and explosibility of metal powders.—See B., 1944, I, 144.

Catalytic action of ozone in the slow combustion of paraffins. Ozonisation of the terminal groups of the saturated hydrocarbons of the aliphatic series. J. Carceller Fernández (*Anal. Fis. Quím.*, 1940, 36, 235—240; cf. A., 1935, 1103, 1466).— O_3 accelerates the oxidation of C_2H_6 , C_3H_8 , C_4H_{10} , and C_5H_{12} to $RCHO$ and RCO_2H (R = alkyl), CO , H_2O , and peroxides. The ease of oxidation \propto mol. wt. of the paraffin. Fission of the C chain represented by CO and H_2O is for *iso*- > for *n*- C_4H_{10} , and increases with the higher members of the series. The chain mechanism is favoured to explain the reaction. F. R. G.

Hydrocarbon polymerisation and method of determining catalyst activity. R. F. Cane (*J. Proc. Austral. Chem. Inst.*, 1943, 10, 279—286).—A review of existing theories of the action of H_2PO_4 as catalyst for the polymerisation of unsaturated hydrocarbons shows these to be untenable. The suggested procedure for determining the activity of polymerisation catalysts involves mixing 50 g. of α -phellandrene with 20 g. of catalyst at 20° in a Dewar vessel of known H_2O -equiv. and cooling correction, the temp. being observed at 1-min. intervals for 5 min. and thence at 5-min. intervals for 30 min. The time required for the evolution of 10 g.-cal. per g. of catalyst is called the "activity no." H_2O on the catalyst decreases its activity whilst adsorbed O_2 causes initial acceleration of the polymerisation followed by a retardation. Basic N compounds (NH_3 , amines, nitriles, or C_3H_5N) depress the activity of the catalyst whilst NO_2 -compounds have little or no effect. Traces of mercaptans decrease the activity considerably. J. W. S.

Properties of chromic oxide gel and its catalytic activity for the aromatisation of *n*-heptane. E. J. Dickinson (*Trans. Faraday Soc.*, 1944, 40, 70—79).— Cr_2O_3 gel is reduced by dry H_2 at 450° to an extent corresponding with $\sim 6\%$ conversion into Cr and some H_2 is irreversibly absorbed, whereas at 800° the irreversible absorption is negligible but the reduction is greater (10–5% conversion) than at 450° . There is evidence that in this reduction no new phase is formed, and that the product is Cr_2O_3 from which some O atoms have been removed without collapse of the lattice structure. The reduced gel is completely oxidised by O_2 at 450° , all combined H being removed as H_2O . H_2O oxidises only a small fraction of the reduced gel at 450° , and some H_2O is reversibly adsorbed. It is thought that the part of the gel attacked by H_2O is identical with the part catalytically active in the dehydrogenation of hydrocarbons. The poisoning action of O_2 , H_2O , and oxidation products of hydrocarbons is probably due to "saturation" of the active parts of the gel, the effect of H_2O being temporary owing to its adsorption being reversible. Restoration of the activity of the poisoned gel includes the removal of carbonaceous material and re-forming of the active part of the surface, and is best effected by treatment at 600° first with O_2 and then with H_2 . The pressures employed in these experiments were ~ 3 –4 mm. F. L. U.

Ethylation of benzene. Course of the reaction.—See A., 1944, II, 155.

Interaction of carbon monoxide with [Fischer-Tropsch] cobalt catalyst used in synthesis of gasoline from water-gas.—See B., 1944, I, 158.

Catalytic cracking of oils.—See B., 1944, I, 126, 127.

[Catalytic] hydrogenation and liquefaction of coal.—See B., 1944, I, 156.

Behaviour of metals in nitric acid. U. R. Evans (*Trans. Faraday Soc.*, 1944, 40, 120—130).—By considering the attack of HNO_3 on metals to be composed of an anodic reaction, e.g., $M + 2e = M^{2+}$, and a cathodic reaction, the principal facts regarding their behaviour can be explained without special assumptions other than that those reactions are most probable that involve fewest mols. Two such reactions are (1) $NO_2 + e = NO_2^-$ and (2) $HNO_2 + HNO_3 = 2NO_2 + H_2O$, according to which the attack on metals such as Cu, Ag, or Hg will be autocatalytic and will start when a trace of NO_2 is present. The influence of vol. of liquid, stirring, and production of NO is discussed. The behaviour of Fe depends on the formation of a coherent film of Fe_2O_3 which is not attacked by HNO_3 , but can be reduced to Fe^{2+} when the acid is sufficiently dil. to produce H. If a high enough % of Cr is alloyed with the Fe a protective film of Cr_2O_3 is formed, which remains unattacked in dil. HNO_3 since Cr^{III} compounds are not stable. F. L. U.

Effect of salts of mercury, tin, and lead on the cathodic process in zincate electrolytes.—See B., 1944, I, 172.

Electrochemical deposition of tin from solutions of tin compounds.—See B., 1944, I, 172.

Strip steel electroplating with tin, using a sodium stannate bath.—See B., 1944, I, 172.

Current efficiency in a series of electrolytic cells.—See B., 1944, I, 164.

Electrodeposition of manganese from a sulphate bath.—See B., 1944, I, 172.

Mercury-sensitised reaction between hydrogen and nitric oxide. H. A. Taylor and C. Tanford (*J. Chem. Physics*, 1944, 12, 47—52).—The rate of reaction of at. H, produced by Hg sensitisation, with NO is $\propto [H]$ at low $[H_2]$, and $<$ proportional at higher $[H_2]$. [NO] is without influence except when NO is in excess, when it retards the reaction. At const. total pressure there is a max. rate with a particular excess of H_2 . HNO radicals are probably formed and decompose on the wall to N_2O , which is rapidly reduced to N_2 . L. J. J.

Photochemical studies in gels. I. Reduction of ferric chloride by mandelic acid in light of different frequencies in thorium phosphate gel as a solvent medium. J. C. Ghosh and S. K. Bhattacharyya (*J. Indian Chem. Soc.*, 1943, 20, 377—381).—The reaction, studied for frequencies 366 and 436 $m\mu$, is zero-mol., and the velocity coeff. increases with rise in concn. of $FeCl_3$ or of mandelic acid (I) and \propto intensity of absorbed radiation; the quantum efficiency is very low. The reaction rate is the same in both sol and gel states of Th phosphate but in H_2O it is much greater. Extinction coeffs. of $FeCl_3$ in excess of (I) measured in all three media are tabulated. A mechanism is suggested. N. M. B.

Photochemical chlorination and photochemical oxidation of tetra-chloroethylene sensitised by chlorine. C. Schott and H. J. Schumacher (*Z. physikal. Chem.*, 1941, B, 49, 107—125).—The photochemical chlorination of C_2Cl_4 to C_2Cl_6 proceeds according to $d[C_2Cl_6]/dt = k[I_{abs.}]^{1/2}[Cl_2]$. At 80° with 100 mm. of Cl_2 and $= 1.6 \times 10^{12}$ $hv/sec. cm.^2$ the quantum yield is 340 mols. per hv . Increase of the total pressure and addition of SO_2 do not affect the reaction. The temp. coeff. is 1.33 per 10° rise in temp., which leads to an activation energy for the total reaction of 7.35 kg.-cal. per g.-mol. The reaction proceeds via the free radical C_2Cl_5 . The oxidation of C_2Cl_4 sensitised by Cl_2 , in which $\sim 80\%$ and 20% of the C_2Cl_4 , respectively, are converted into CCl_3COCl and $COCl_2$, proceeds according to $dp/dt = [I_{abs.}][O_2]/(k' + k''[O_2])$. At 60° with 100 mm. of Cl_2 , 200 mm. of O_2 , and $I_{abs.} = 1.6 \times 10^{12}$ $hv/sec. cm.^2$, the quantum yield is 230 mols. per hv . The temp. coeff. of the reaction is ~ 1.0 . The total pressure has little effect on the reaction. Addition of EtOH causes strong inhibition. Mechanisms for the two reactions are proposed. The results are compared with the corresponding reactions of C_2HCl_3 . J. F. H.

Application of probability considerations to the mechanism of the photochemical polymerisation of acetylene. B. L. Dunicz (*J. Chem. Physics*, 1944, 12, 37—45).—Quantum yields and heats of reaction in fair agreement with the author's experimental results (A., 1941, I, 480) are obtained by assuming equal probabilities for the formation of products of addition and breaking down of single C-C linkings in the unstable intermediate products. L. J. J.

Photolysis of methylamine. O. C. Wetmore and H. A. Taylor (*J. Chem. Physics*, 1944, 12, 61—68).—Photolysis of NH_2Me at 100° irradiated with a low-pressure Hg arc proceeds by two consecutive reactions: H_2 , NH_3 , and CH_3NMe are first formed, and the latter is dehydrogenated. Both reactions are first order, the rate coeff. of the second being approx. double that of the first. The final product has the approx. composition C_2H_3N . H atoms react with NH_2Me and are involved in the reaction. L. J. J.

Relations between chemical activity and absorption in the ultra-violet of certain organic molecules. III. Velocity of replacement of the chlorine atoms in the chloro-derivatives of the substituted amides of malonic acid. K. G. Naik, R. K. Trivedi, and C. M. Mehta (*J. Indian Chem. Soc.*, 1943, 20, 365—368).—Investigations show that the velocity curves are in general agreement with those of absorption in the ultra-violet, the velocity is augmented by the presence of Me in the C_6H_5 nucleus, the Cl atoms of the Cl_2 -derivatives are replaced in succession, and the aliphatic straight chain attached to the CO groups increases the rate of replacement. N. M. B.

Photolysis of the *d*-glycosides: α -benzylfructofuranoside, β -benzylfructopyranoside, and α - and β -phenyl-, -benzyl-, and β -phenyl-ethyl-glycosides; and the bearing of the data on the transfer of energy within molecules. L. J. Heidt (*J. Franklin Inst.*, 1942, 234, 473—485; cf. A., 1939, I, 620).—The absorption spectrum of freshly prepared fructose has a deeper min. at λ 240 $m\mu$. than previously reported vals. The latter were approached with old samples, although no change in sp. rotation or m.p. had taken place. The absorption spectra of α -benzylfructofuranoside and β -benzylfructopyranoside are almost identical, in the near ultra-violet, with those of benzyl-glycosides and CH_2Ph-OH . Aq. buffered solutions of the glycosides were photolysed with monochromatic light of λ 254 $m\mu$. The products were examined for reducing material with the alkaline Cu^{II} reagent of Shaffer, Hartmann, and Somogyi, and for optical activity with a polarimeter. The products of photolysis are, in general, identical with those obtained by thermal hydrolysis; the β -glucos-

ides and α -fructosides, however, yield optically inactive photolytic products. <5% of the light absorbed produces reaction. The above results lead to the hypothesis that the photochemical reaction is produced by an intermol. transfer of the absorbed energy from the aglycone to the hemiacetal O-bridge, which is the reactive centre. J. F. H.

Radiochemistry. A review of recent progress. C. B. Allsopp (*Trans. Faraday Soc.*, 1944, 40, 79—87). F. L. U.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Method of obtaining fresh water from salt [by distillation]. T. Jefferson (*J. Chem. Educ.*, 1943, 20, 575—576). L. S. T.

Enrichment of chlorine isotopes by irradiation of chlorine dioxide at low pressure. W. Kuhn, H. Martin, and K. H. Eldau (*Z. physikal. Chem.*, 1941, B, 50, 213—254).—Pure ClO_2 at ~ 0.2 mm. pressure, when irradiated with $\lambda\lambda$ 3650.15, 3654.83, and 3663.27 \AA , is decomposed without reaction chain formation and with quantum yield ~ 1 to Cl_2 and O_2 . The Cl_2 liberated has at. wt. $0.016 <$ that of normal Cl . The small degree of isotope separation is due to the coincidence of only the last-named of the above lines with a $^{35}\text{ClO}_2$ absorption band. The other two lines have intensities ~ 4 times greater. L. J. J.

Separation of radiothorium and radium-D and the purification of radium-mesothorium salts. B. A. Nikitin and A. E. Polesitzki (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 494—497).—Distillation in HCl at 800° effects complete separation of Ra-Th and Th-B or Ra-D from Ba salts. Further heating at 600° in HCl causes volatilisation of Th-B and Ra-D, whilst Ra-Th remains. The method can be used for the purification of Ra and for the regeneration of Ra from metallic hydroxides containing adsorbed Ra, since FeCl_3 , AlCl_3 , and ThCl_4 are all volatile in HCl whilst RaCl_2 is non-volatile. J. W. S.

Constitution of "pernitrous acid." I. A. Rius and O. R. Foz (*Anal. Fis. Quim.*, 1940, 36, 308—321).—Potentiometric measurements show that [active O] = $[\text{NO}_2]$ in pernitrous acid. Decomp. by alkali yields nitrites and is accelerated by H_2O_2 and light. F. R. G.

Chemistry of polonium. II. Preparation of hexavalent polonium. A. G. Samartzeva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 498—501).—By observations on the distribution of Po between crystals of $\text{K}_2\text{TeO}_4 \cdot 3\text{H}_2\text{O}$ (I) and its saturated solution, both in presence and in absence of K_2PO_4 , it has been shown that Po crystallises isomorphously with the Te compound and enters the crystal lattice of (I). Hence Po can yield hexavalent compounds derived from H_2PoO_4 . J. W. S.

New sources of bromine.—See B., 1944, I, 133.

Reaction between ferrous sulphide and cupric sulphide in the solid state, at room temperature. H. Forestier and (Mlle.) J. Longuet (*Compt. rend.*, 1942, 215, 439—440).—By addition of aq. Na_2S to a solution of equimol. proportions of FeCl_2 and CuCl_2 , at room temp., a ppt. is obtained which, after drying in vac. over P_2O_5 , gives the Debye-Scherrer X-radiogram of chalcopyrite (I); sharper and stronger X-ray lines are obtained if the aq. suspension is boiled for 15 hr. prior to filtration. (I) is also obtained after mixing suspensions of FeS and CuS , showing that copptn. of the sulphides is not essential to their combination. FeS and CuS combine more readily than FeO and CuO (cf. A., 1939, I, 482; 1942, I, 276, 336). A. J. E. W.

Hydrogen dihydroxotetrachloroplatinate as a reagent for tin. I. G. Fesenko (*Zavod. Lab.*, 1939, 8, 1323—1324).—The compound $\text{Sn}[\text{PtCl}_4(\text{OH})_2]$ (cf. Chotulev, A., 1939, I, 41) does not exist. J. J. B.

X.—LECTURE EXPERIMENTS AND HISTORICAL.

Wetting and spreading. Laboratory experiment [with lauric acid]. L. J. Bircher (*J. Chem. Educ.*, 1943, 20, 428—430). L. S. T.

Autocatalytic experiment to illustrate virus growth. P. Hersch (*J. Chem. Educ.*, 1943, 20, 376).—Conditions under which the reduction of $\text{Ni}(\text{OH})_2$ to Ni by H_2PO_4^- can be made to resemble the growth of bacterial colonies on a culture medium are described. L. S. T.

Thomas Jefferson's relation to chemistry. C. A. Browne (*J. Chem. Educ.*, 1943, 20, 574). L. S. T.

Benjamin Chew Tilghman, and the origin of the sulphite process for delignification of wood. M. Phillips (*J. Chem. Educ.*, 1943, 20, 444—447). L. S. T.

M. Carey Lea, chemist, 1823—1897. E. F. Smith (*J. Chem. Educ.*, 1943, 20, 577—579). L. S. T.

Jacob Green, chemist, 1790—1841. E. F. Smith (*J. Chem. Educ.*, 1943, 20, 418—427). L. S. T.

Franklin Bache, chemist, 1792—1864. E. F. Smith (*J. Chem. Educ.*, 1943, 20, 367—368). L. S. T.

Scientific and technical work of A. G. Green. K. H. Saunders (*J. Soc. Dyers and Col.*, 1944, 60, 81—93).

XI.—GEOCHEMISTRY.

Presence of phosphorus in the solar atmosphere. K. N. Rao (*Indian J. Physics*, 1943, 17, 197—203).—The presence of P_2 in the solar atm. is inferred from coincidences of the lines of two of its strong bands (8,27 and 9,28) with the Fraunhofer lines. W. R. A.

New method of measuring the mean height of the ozone in the atmosphere. K. Watanabe (*J. Franklin Inst.*, 1943, 236, 461—471).—Measurements made and results obtained by Strong's method (cf. A., 1940, I, 310) are reported and discussed. N. M. B.

Isotopic composition of oxygen of different origin. A. P. Vinogradov and R. V. Teis (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 33, 490—493).—Determinations of the d of H_2O synthesised from H_2 (produced by the action of HCl on Zn) and O_2 from various sources indicate that O from the atm. is heavier than that from H_2O whilst that evolved under the action of light by *Helodea canadensis* growing in tap- H_2O containing 0.1% of NaHCO_3 is intermediate. The O in CO , produced by the action of HCl on NaHCO_3 , is heavier than atm. O. J. W. S.

Pentathionic acid in water from Copahue. H. Corti and R. J. Manuele (*Rev. Fac. Cienc. Quim., La Plata*, 1942, 17, 7—14).—A sample of H_2O collected from the volcano of Copahue (Chile) 22 years earlier contained 0.688% of $\text{H}_2\text{S}_5\text{O}_6$ and 0.07% of As_2O_3 . $\text{S}_2\text{O}_6^{2-}$ is attributed to atm. oxidation of suspended S. F. R. G.

Chlorophyll content and productivity in lakes in N.E. Wisconsin.—See A., 1944, III, 380.

Sediments of four woodland lakes, Vilas Co., Wisconsin. II. W. H. Twenhofel, V. E. McKelvey, S. A. Carter, and H. Nelson (*Amer. J. Sci.*, 1944, 242, 85—104).—The dominant and most abundant form of org. sediment is a pale greenish-yellow gel of small globules. The composition of the various sediments is described. L. S. T.

Recent deposits of vesiculated mud along south-western Ohio streams. R. H. Griffin and R. E. Shanklin (*J. Geol.*, 1943, 51, 488—494).—Calcareous silts deposited along these streams contain a high proportion of finely-divided, partly-digested org. matter, mainly sewage. Desiccation is accompanied by vesiculation as gases are generated by decomp. of org. matter, and by reaction of org. acids formed during decomp. with carbonate in the mud. L. S. T.

Factors influencing the distribution of the elements. J. H. Pannell (*Amer. Min.*, 1943, 28, 605—613).—A discussion. L. S. T.

New type of stichtite found in the serpentine massif of Bou-Oufroh, Morocco. (Mlle.) S. Caillère (*Compt. rend.*, 1942, 215, 420—422).—Analyses [by R. Frey and J. Burghelle] of the mineral (cf. A., 1934, 386) are: CO_2 7.86, 8.50; FeO 0.31, 0.16; Fe_2O_3 13.90, 14.18; Al_2O_3 2.08, 2.06; Cr_2O_3 6.19, 4.92; MgO 37.34, 38.26; $\text{H}_2\text{O} + 32.52$, 31.92%. These give the composition $9\text{MgO}(\text{Fe,Cr})_2\text{O}_3 \cdot 2\text{CO}_2 \cdot 18\text{H}_2\text{O}$. Optical properties (including n_g 1.562, n_p 1.543) are summarised. Identity with stichtites from Tasmania and Transvaal is confirmed by thermal and X-ray analysis, the Fe content indicating a passage from stichtite to brugnatellite and pyroaurite. A. J. E. W.

Associations of heavy minerals in certain post-Cretaceous formations in the Paris basin (region south of the Seine). B. Bräjniov (*Compt. rend.*, 1942, 215, 491—493).—The occurrence of characteristic groups of associated minerals is discussed, and the petrological significance of the appearance of augite is noted. A. J. E. W.

Spectroscopic study of the mineral deposits of Kazakhstan with regard to the content of rare and scattered elements. S. K. Kalinin (*Bull. Acad. Sci. U.R.S.S., Sér. phys.*, 1941, 5, 253—255).—A short review of work on the minerals of Kazakhstan to determine the distribution of rare and scattered elements. Deposits enriched in Ga, In, Tl, Ge, and other elements have been discovered. R. C. P.

Brucitic limestones and hastingsite syenite near Wakefield, Quebec. I. J. W. Ambrose (*Trans. Roy. Soc. Canada*, 1943, [iii], 37, IV, 9—22).—Occurrence is described, and chemical analyses are recorded and discussed. The amount of brucite (I) in the purer varieties of brucitic limestone ranges between 20 and 30%. The syenite has played an essential role in producing (I) and the history of these limestones is sedimentary limestone, dolomitisation, intrusion of syenite, dedolomitisation with formation of periclase (II), and hydration of (II) to (I). L. S. T.

Morphology of carborundum. J. D. H. Donnay (*Trans. Roy. Soc. Canada*, 1943, [iii], 37, IV, 43—47).—The theoretical significance of the morphology of carborundum is discussed. The dependence of the external forms on the internal structure is illustrated, and is considered to be the final indictment of Goldschmidt's views on normal form-series. L. S. T.

Gold-silver ratios in certain Ontario gold mines. E. L. Bruce (*Trans. Roy. Soc. Canada*, 1943, [iii], 37, IV, 23—31).—The Au : Ag ratios of the bullion from 7 mines are recorded graphically and are discussed. In some deposits the Au : Ag ratio appears to decrease with depth. The ratio differs for different kinds of wall rocks even on the same level. Ag shows less variation than Au.

L. S. T.

Yorkshire Dogger. III. Upper Eskdale. R. H. Rastall and J. E. Hemingway (*Geol. Mag.*, 1943, 80, 209—230; cf. A., 1942, I, 251).

L. S. T.

Self-diffusion in minerals, particularly copper sulphides. A. M. Gaudin and K. C. Vincent (*Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1663, 6 pp.; *Min. Tech.*, 8, No. 1: cf. A., 1936, 424).—It has previously been found that chalcocite (I) abstracts Cu⁺ xanthate from C₆H₆ solution, and that the xanthate cannot be removed by leaching. Experiments have been made by the method of radioactive indicators to determine whether Cu diffuses into (I) from the xanthate. Radioactive solutions of Cu, Zn, and S were agitated with powders of natural (I), azurite (II), tetrahedrite (III), and sphalerite (IV), and synthetic (I) and covellite (V). The radioactivity of the solution and mineral, before and after contact with one another, was determined. The minerals acquired no radioactivity from the Zn or S solutions, but (I), and to a smaller degree (II), (III), and (V), became radioactive in the Cu solution. (IV) did not show this effect. Apparently in (I) the solid consists of two entities—S which is immobile, and Cu which is wandering freely.

C. E. H.

Chemical relationship of cryptomelane (psilomelane), hollandite, and coronadite. J. W. Gruner (*Amer. Min.*, 1943, 28, 497—506).—These minerals are isostructural and form isomorphous mixtures. The unit cell of the group contains 16 O ions, and has the formula

$Mn^{IV}_8 - (x/2 + y/4 + z/2)(Mn^{II}, R^{II})_x(K, Na)_y(Ba, Pb)_{z/2}16O_2(H_2O)_2 - (y + z)$. K, Ba, and Pb occupy identical positions, and the ratio $x : y : z$ depends on the state of oxidation of Mn, which, in turn, depends on the conditions under which the mineral is formed. H₂O occupies positions that could be filled by K, Ba, or Pb. The mineral originally named romanechite by Lacroix consists of minute crystals of cryptomelane. X-Ray powder spectra are compared.

L. S. T.

South-Western end of the Newry igneous complex. Petrogenesis of the granodiorites. D. L. Reynolds (*Quart. J. Geol. Soc.*, 1943, 99, 205—246).—Chemical analyses are recorded, and chemical changes involved in the petrogenesis of hornblende-, biotite-, and porphyritic granodiorite discussed.

L. S. T.

Portencorkie complex of Wigtownshire. N. Holgate (*Geol. Mag.*, 1943, 80, 171—195).—Chemical analyses of adamellite and a pyroxene-mica-diorite are given.

L. S. T.

Intrusive rocks of the Shelve area, South Shropshire. F. G. H. Blyth (*Quart. J. Geol. Soc.*, 1943, 99, 169—204).—The intrusions range from picrite to alkali-rich andesite; their structure and petrology are described. Chemical analyses are recorded.

L. S. T.

Migmatite area around Bettyhill, Sutherland. Y.-C. Cheng (*Quart. J. Geol. Soc.*, 1943, 99, 107—154).—The migmatization of pelitic, semi-pelitic, siliceous, and hornblende rocks of the Moine Series is a record of a lengthy series of metasomatic changes brought about by the activity of alkaline solutions. Variation diagrams and chemical analyses are recorded and discussed.

L. S. T.

Fibrous sepiolite from Yavapai Co., Arizona. A. J. Kauffman, jun. (*Amer. Min.*, 1943, 28, 512—520).—Chemical analyses, optical and X-ray data identify a hydrous Mg silicate from this locality as fibrous sepiolite (I). Well-cryst. specimens of (I), free from impurities, have lower v and better defined X-ray patterns than those containing amorphous material. The continued use of the term "parasepiolite" when referring to the highly cryst. variety of this mineral is recommended.

L. S. T.

Phase equilibrium in the system Li₂O-Al₂O₃-SiO₂.—See A., 1944, I, 128.

Unidentified mineral in the quartz basalt [at Cinder Cone], Lassen Volcanic National Park, California. R. Merriam and T. G. Kennard (*Amer. Min.*, 1943, 28, 602—604).—Occurrence of a light-blue glass and a blue-green mineral, α 1.545, β 1.565, γ 1.675 (± 0.002), ρ 2.60 ± 0.02 , hardness 3, is described. Spectrographic analyses of glass and mineral show the presence of Al, Si, small amounts of Ca, Mg, Fe, Cu, and traces of Li, Na, B, Ba, Mn, Pb, and Ti.

L. S. T.

Calculation of molecular formulæ for glauconite. C. O. Harvey (*Amer. Min.*, 1943, 28, 541—543).—The procedure described by Hendricks and Ross (*ibid.*, 1941, 26, 683) is unnecessarily elaborate. A shorter method is given. A chemical analysis of glauconite obtained from a sand at Chobham, Surrey, is recorded.

L. S. T.

New data on agricolite, bismoclite, koechlinite, and the bismuth arsenates. C. Frondel (*Amer. Min.*, 1943, 28, 536—540).—Agricolite is identical with eulytite, and rhagite with atlestite (I). Arseno-

bismite (II) from Tintic, Utah, is a valid species; a new locality for it is at Tazna, Bolivia. A new, unnamed Bi arsenate, which alters to (II), occurs abundantly in association with (II) at the Mammoth mine in the Tintic district, Utah. X-Ray powder data for (I), (II), koechlinite, and the new Bi arsenate are tabulated.

L. S. T.

Two andalusite pegmatites from Riverside Co., California. R. W. Webb (*Amer. Min.*, 1943, 28, 581—593).—Reported occurrences of andalusite (I) in pegmatite are reviewed, and two new occurrences in which (I), corundum, microcline, and quartz are found in giant intergrowths, in metamorphic terrains, are described. Geological setting and genesis are discussed.

L. S. T.

Pegmatite crystallisation. T. T. Quirke and H. E. Kremers (*Amer. Min.*, 1943, 28, 571—580).—The geological, physical, and chemical conditions that control the pptn. and growth of pegmatite minerals are discussed.

L. S. T.

Internal structure of silicate minerals that gelatinise with acid. K. J. Murata (*Amer. Min.*, 1943, 28, 545—562).—A list of silicate minerals reported to gelatinise on being treated with acid is arranged according to a classification based on the internal structures of the minerals. Examination of the data indicates that the following classes of minerals, if vulnerable to acid attack, will gelatinise: (1) minerals containing silicate radicals of small mol. wt., viz., orthosilicates, pyrosilicates, and possibly silicates containing ring structures of three Si atoms, (2) minerals with large continuous Si-O networks that will disintegrate into units of low mol. wt., (a) disilicates containing much Fe^{III} in the Si-O sheets, (b) minerals of the SiO₂ type with 3-dimensional networks that contain <2Al to 3Si. Minerals that separate insol. SiO₂ instead of gelatinising on treatment with acid are characterised by Si-O structures of large dimensions that do not disintegrate into small units under acid attack. These are SiO₂ chains, Si₂O₁₁ double chains, Si₂O₆ sheets not containing large amounts of Fe^{III} replacing Si, and 3-dimensional networks with <2Al to 3Si. Exceptions to these rules are discussed.

L. S. T.

Mineralogy of the oxides and carbonates of bismuth. C. Frondel (*Amer. Min.*, 1943, 28, 521—535).—Bismutite, (I), ρ 6.61—7.33, Bi₂CO₃, supposedly a hydrate, contains only non-essential H₂O. On heating, (I) and artificial Bi₂CO₃. n H₂O lose H₂O gradually to ~290°, when CO₂ is lost, and α -Bi₂O₃ remains. Artificial hydrates of Bi₂CO₃ are unknown. 46 proven localities for (I) are given. Bismutospherite and basobismutite, and probably hydrobismutite and normannite, are identical with (I). Walthierite (II), a Bi carbonate of unknown formula, is a distinct species, monoclinic with c_0 5.42 \pm 0.05 Å.; ρ 5.32. Beyerite (III) is the name given to a new Bi Ca carbonate of unknown formula. (III), a_0 3.78 \pm 0.01, c_0 21.77 \pm 0.05 Å., ρ 6.56, hardness >3, space-group type, primitive, occurs at the Stewart mine, Pala, California, as compact greenish-grey masses embedded in quartz. The crystals are small, thin yellow plates. (III) contains traces of Si, Al, Mn, Pb, Mg, Cd, and Cu. The name bismite (IV) should be restricted to the α -polymorph of Bi₂O₃. Sillenite (V), is the name given to a body-centred isometric polymorph of Bi₂O₃ found as a secondary product at Durango, Mexico. Evidence for the existence of a definite hydrate of Bi₂O₃ in nature is reviewed, and a probable occurrence of Bi₂O₃.3H₂O is described. X-Ray powder spacing data and photographs for (I), (II), (III), (IV), and (V) are given. (See also C., 1944, Part 3.)

L. S. T.

Crystal chemistry and geochemistry. Applications for recovery of rare elements in science and industry. V. M. Goldschmidt (*Chem. Products*, 1944, 7, 29—34).—A lecture dealing with the distribution of elements in nature. The size of atoms and ions as the controlling factor in distribution is emphasised, and it is shown how a knowledge of these magnitudes makes it possible to predict the occurrence of elements. The "camouflage" of elements, i.e., the fact that a rare element with approx. the same at. radius as a more common one may exist with the latter and remain undetected (e.g., Ga and Al; Hf and Zr), is discussed. The effect of bond strength on sequence of crystallisation is dealt with.

A. J. M.

Thermal analysis of clay minerals.—See B., 1944, I, 133.

Nevis oil-shale deposit, Nevis Survey District, Otago Central. R. W. Willett (*New Zealand J. Sci. Tech.*, 1943, 24, B, 239—254).—The geology of the deposits, their extent, physical properties, chemical composition, and exploitation are described.

L. S. T.

Oil shales at Cambrian, Freshford, and Waitati, Otago and Southland. R. W. Willett (*New Zealand J. Sci. Tech.*, 1943, 24, B, 255—271).—Previous work on these deposits is reviewed, available chemical analyses are recorded, and geology of the deposits is described. Estimates of probable quantities are given.

L. S. T.

Mode of preservation of plant fossils and its bearing on the problem of coal formation. A. Kryštofovich (*Amer. J. Sci.*, 1944, 242, 57—73).—Some of the special types of plant preservation that throw light on the alteration of plant tissues into coal are discussed.

L. S. T.

A I—General, Physical, and Inorganic Chemistry.

JULY, 1944.

I.—SUB-ATOMICS.

Structure of λ 5461 of mercury (^{198}Hg). J. H. Wiens (*Physical Rev.*, 1944, [ii], 65, 58).—Spectrograms show no structure for the ^{198}Tl line, but structure is clearly visible in the spectrogram for mixed Hg.

Temperature classification of gadolinium lines. A. S. King (*Astrophys. J.*, 1943, 97, 323—380).— $\lambda\lambda$ and temp. classifications for 5775 lines of Gd from λ 2135 to λ 10677 Å. are given. The temp. classification, including segregation of the lines of Gd I and Gd II, was obtained by comparing the spectra of the C-tube furnace at three temp. with those of the arc and spark. The spectra in successive λ regions are described. In the solar spectrum ~60 lines of Gd II are present, about half of them arising from low at. levels.

Values of the energy of the electronic configuration $3d^2 4p$. M. T. Antunes (*Portugaliae Physica*, 1944, 1, 1—13; cf. A., 1943, I, 45).—Mathematical. The matrix of electrostatic interactions and orbit spin of the $d^2 p$ state is calc. Calc. and empirical vals. of the energy of the $3d^2 4p$ configuration of Ti II are given. The calc. vals. agree well with those assigned by Russell (cf. A., 1928, 679) to the energies of the various levels.

Structure of Th II spectrum. I. F. L. de Bruin, P. Schuurmans and P. F. A. Klinkenberg (*Z. Physik*, 1943, 121, 667—678).—More than 1900 lines are identified as transitions between two term systems in the spectrum of Th⁺, by λ and Zeeman-effect measurements. One system contains 36 odd and 94 even, the other 25 even and 77 odd, terms. The odd terms are ascribed to the $5f7s^2$, $5f6d7s$, and $5f6d$ configurations of Th II. The coupling of 7s electrons corresponds approx. with the $j-j$ type. Only tentative allocation of even terms is possible.

Term values of X-ray spectra. T. M. Hu (*Physical Rev.*, 1944 [ii], 65, 76—79).—The term vals. of K , L , and M levels of X-ray spectra are given by the empirical formula $v(nj) = (1/n^2)[Z - \sigma_0 - \phi(Z)] + (1/n^2)a^2(Z - \sigma_2)^4\{[n/(j + \frac{1}{2}) - \frac{1}{2}] + \dots - \sum_i Z_i [(Z - S_i)/n_i]\}$ where σ_0 and σ_2 are consts. for a given level and $\phi(Z) = -0.098 - 1.80 \times 10^{-3}Z + 1.40 \times 10^{-4}Z^2$ for the K and L levels, and zero for the M level. Vals. for the screening consts. best suited to the formula are given.

Continuous X-ray spectrum. R. Weinstock (*Physical Rev.*, 1944, [ii], 65, 150).—Mathematical note to experimenters. It is suggested that, unless angular distribution is sought, future intensity measurements be made at $50^\circ 44'$ with the (forward or reverse) direction of electron bombardments, provided the apparatus is not thereby rendered unwieldy.

Lead equivalent of thorium with respect to X-rays and radium γ -radiation. R. Jaeger (*Physikal. Z.*, 1943, 44, 153—156).—The Pb equiv. of Th (d 11.4 and 11.7) with respect to X-rays from a tube working at 15—300 kv. has been determined for 10 different hardnesses, and various thicknesses of Pb and Th filters. In general 1 mm. of Th corresponds to >1 mm. of Pb, but for effective $\lambda\lambda$ lying between the K and L absorption edges of Th and Pb 1 mm. of Th corresponds to ~0.7 mm. of Pb. The max. val. is 1.65 mm. of Pb equiv. to 1 mm. of Th, and occurs for λ 0.25 Å. Hard γ -rays from Ra-C give 1.16 mm. of Pb equiv. to 1 mm. of Th.

Quadratic Zeeman effect of the europium sulphate lines. A. Schmillen (*Ann. Physik*, 1941, [v], 39, 502—511).—The transverse Zeeman effect has been investigated with single crystals of $\text{Eu}_2(\text{SO}_4)_3$ with various orientations and with polarised light. The lines of the blue and green absorption groups, corresponding to transitions $^3F_0 - X_2$ and $F_0 - X_1$, show a Zeeman effect \propto (field strength)². The magnitude and direction of the effect are independent of the direction of the light, and the polarisation depends only on the orientation of the field with respect to the crystal. From the intensities of the absorption lines for different directions of the light and of the polarisation, conclusions about the direction of vibration of the absorbing dipoles may be drawn. The absorption of the blue group is ascribed to electric dipoles, some of which are vibrating in a definite direction, others in a single plane, and others in unspecified directions. The absorption of the green group is due to magnetic dipoles which vibrate in one direction.

A. J. M.

Photo-electric conductivity of zinc sulphide-copper phosphors under the influence of α -rays. F. Lappe (*Ann. Physik*, 1941, [v], 39, 604—618).—Photo-electric determinations, especially dealing with the secondary current, are made on untreated ZnS-Cu phosphors, and on phosphors which have been irradiated with α -rays. To obtain measurable and reproducible currents on illumination the thinnest possible layers must be used. The inertia of the decay of the illumination current decreases with potential. The extinction effect of illumination of λ 500—900 m μ . is investigated. The effect on a phosphor that has been illuminated for some time is considerable. The decrease of current caused by the extinction effect reaches a saturation val. similar to excitation. The effect of α -rays on the current is investigated. There is considerable inertia. The effect of simultaneous distortion of the centres on the current is also investigated. The effect of increasing distortion on the illumination current is approx. linear. The effect of extinction on the secondary current increases linearly with the distortion. In this case the extinction effect extends over all $\lambda\lambda$. There is a marked effect of pressure on the secondary current. The dark- and the light-current increase considerably at small pressures, owing to the effect of adsorbed gas on the transition of electrons between the micro-crystals.

A. J. M.

Absorption of thorium on tantalum. C. J. Gallagher (*Physical Rev.*, 1944, [ii], 65, 46—50).—Th was evaporated from thoriated W on to a well-outgassed Ta ribbon, and the thermionic emission at 1390 K. was studied as a function of the time of evaporation. The work function of the ribbon decreased from 4.07 to 2.52 v. and the emission const. decreased by a factor 30. Qual. results are analogous to those for Th on W or Mo. A study of the emission from the two sides of the ribbon at 1550° K. showed a decrease from the activated side and an increase on the clean side, to equilibrium after 24 hr. indicating that the adsorbed Th had migrated around the edges of the ribbon and distributed itself uniformly over the emitting surface.

M B

Directional distribution of X-ray intensities from massive anticathodes. H. Hinz (*Ann. Physik*, 1941, [v], 39, 573—590).—The intensity distribution is investigated for anticathodes of Be, Al, Cu, Ag, and Pb, at 150—300 kv. For Be the potential necessary to separate the intensity max. is determined, the position of the max. being followed with increasing filtering up to 250 kv. At this potential, the observed val. is $\sim 9^\circ$ < that deduced from Sommerfeld's theory, this discrepancy being explained by cathode-ray diffusion, and the superposition of different parts of the X-ray cone. The difference in intensity (I) of radiation at directions 0° and 90° increases with increased filtering and voltage. I_0/I_{90} decreases with increasing at. no. of the anticathode material, if tube potential and filtering are the same. For Pb, I_0/I_{90} is >1.

A. J. M.

Currents carried by electrons of uniform initial velocity. G. Iaffé (*Physical Rev.*, 1944, [ii], 65, 91—98).—Mathematical.

Interpretation of the spinning electron with bipolar co-ordinates. (Miss) M. H. Payne (*Physical Rev.*, 1944, [ii], 65, 39—46).—Mathematical. A geometrical picture of the Pauli and Dirac spin theories is developed.

N M B

Refractive index in electron optics. I. Opatowski (*Physical Rev.*, 1944, [ii], 65, 54—55).—Mathematical.

N. M. B.

Negative ions of atomic and molecular oxygen. D. R. Bates and H. S. W. Massey (*Phil. Trans.*, 1943, A, 239, 269—304).—The properties, and modes of formation and of destruction, of the negative ions of O and O₂ are examined in detail, with quantum theory interpretation. A detailed examination is made of the $(1s)^2(2s)^2(2p)^4(3s)$ excited configuration of O⁻, and Hartree-Fock equations are solved for the deepest terms, but conflicting results prevent a decision as to the sign and magnitude of the binding energy of the 3s electron. To examine possible reasonable effects, radiative attachment and detachment rates are calc. for various vals. of the polarisability parameter. To interpret attachments of electron swarms in O₂, the deep electronic states of O₂⁻ are examined by empirical methods. The distribution makes it unlikely that O₂⁻ ions can be formed with any probability by attachment of slow electrons to O₂ at low pressures by a pressure-independent process other than direct radiative attachment. The theory of the crossing of mol. potential energy

curves is applied to the formation of oppositely charged ions from mols. by impact of electrons or light quanta, and to determination of the magnitude of cross-section for mutual neutralisation of oppositely charged ions by electron transfer on impact. The most probable val. for O ions is 10^{-12} – 10^{-13} sq. cm. N. M. B.

Analysis of β -ray spectra. A. Gibert (*Portugaliae Physica*, 1944, 1, 15–28).—Experimental facts not readily explained by supposing that β -spectra are due entirely to an internal photo-electric effect are reviewed. The work of Stahel (A., 1933, 205) on a type of coupling between the nucleus and the extranuclear electrons in β -radioactive transformations is considered, and outstanding anomalies are discussed. Stahel's results are in good agreement with more recent determinations. A. J. M.

Einstein's photo-electric law and the phenomenon of internal conversion. M. Valadares (*Portugaliae Physica*, 1944, 1, 35–41).—Comparison of the results obtained for the determination of the $\lambda\lambda$ of γ -rays by the magnetic spectrography of β -rays arising from internal conversion, and by the diffraction of γ -rays at crystals, indicates that the Einstein photo-electric law holds for the internal conversion of β -rays. A. J. M.

Inelastic scattering of slow neutrons. R. Weinstock (*Physical Rev.*, 1944, [ii], 65, 1–20).—Mathematical. The total polycryst. elastic and inelastic scattering cross-sections are calc. by Born's approximation with use of the Fermi interaction between slow neutrons and bound nuclei. Results are applied to scattering by Fe for 0–1000° K. Comparison of results for inelastic scattering with Zachariasen's theory of the diffuse scattering of X-rays is examined. N. M. B.

Angular distribution of alphas from ${}^7\text{Li}$ (p, α). C. D. Swartz, H. H. Rossi, B. Jennings, and D. R. Inglis (*Physical Rev.*, 1944, [ii], 65, 80–82).—The tracks formed in photographic emulsions at various angles from the beam were observed for bombarding energies $E = 400$ – 900 e.v. The angular distribution was $\propto 1 + A(E) \times \cos^2 \theta$, as at lower voltages (cf. Young, A., 1940, 1, 426), and there is a max. of $A(E)$ at 675 kv. N. M. B.

Interpretation of the angular distribution of alphas from ${}^7\text{Li}$ (p, α). E. Eisner (*Physical Rev.*, 1944, [ii], 65, 85–87).—Proton penetration factors are calc. under several assumptions of nuclear potential. The Critchfield-Teller theory is briefly discussed in the light of these calculations and the angular distribution (cf. preceding abstract). N. M. B.

Angular distribution of alphas from ${}^{19}\text{F}$ (p, α) ${}^{18}\text{O}$. H. H. Rossi and C. D. Swartz (*Physical Rev.*, 1944, [ii], 65, 83–85).—The angular distribution, investigated for bombarding energies $E = 500$ – 900 e.v., depends markedly on E , contrary to results at lower voltages (cf. McLean, A., 1940, 1, 426). N. M. B.

Strontium and yttrium isotopes from uranium disintegration. O. Hahn and F. Strassmann (*Z. Physik*, 1943, 121, 729–745; cf. A., 1944, I, 95).—The new 20-min. Y isotope has been identified as a transformation product of a Kr isotope from highly active U preps. Its direct precursor is a Sr isotope of short life, with a half-life of 2–0.5 min., so far not isolated. Half-lives of a no. of Sr and Y isotopes have been more exactly determined than heretofore. L. J. J.

Cascade showers and nuclear disintegrations at 10,000 feet. W. E. Hazen (*Physical Rev.*, 1944, [ii], 65, 67–75).—In 8500 photographs obtained with a large cloud-chamber containing 8 Pb plates and operated without counter control at 10,000 ft., 1090 cascade showers and 58 nuclear disintegrations were observed. The differential energy spectrum for the shower-producing rays is $\propto E^{-1.7}$ for $E = 2 \times 10^6$ e.v., and to $E^{-3.0}$ for $E = 10^9$ e.v. The shower-producing rays with $E > 2 \times 10^6$ e.v. constituted 6.5% of the radiation; $\frac{1}{4}$ of the shower-producing rays were photons. Nuclear disintegrations initiated by neutrons or protons contained Pb-penetrating particles which were mostly protons or mesotrons. N. M. B.

Variation of mesotron intensity with altitude and latitude, together with allied phenomena, and the bearing of these matters on the nature of the primary particles. W. F. G. Swann (*J. Franklin Inst.*, 1943, 236, 1–7, 111–139).—Results stated in condensed form in earlier publications by the author are established, and detailed proofs of some of the formulæ previously cited are given. The min. meson velocity necessary to account for the sea-level latitude ratio and the intensity-altitude data is too high to permit the symmetrical electron emission at death of proton-born mesons indicated by the observed horizontal intensities at high altitudes. To give a sufficiently low meson velocity the incoming primaries also must have a low velocity, which demands a greater mass than the proton. For these primaries charged He atoms are invoked to account for high-altitude phenomena, in addition to the protons already invoked to explain phenomena at low and medium altitudes. The slow mesons born of the charged He atoms die before they penetrate far into the atm. W. J.

Polygonal surface and periodic classification of elements. W. Finke (*Z. Physik*, 1943, 121, 586–587).—Comments on work by G. Haenzel. A representation of electronic quantum nos. of known

at. species in three dimensions, employing cartesian or mixed cartesian-polar co-ordinates, is proposed. L. J. J.

Statistical theory of the atom. P. Gombás (*Z. Physik*, 1943, 121, 523–542).—Interaction of electrons with antiparallel spins is considered. Boundary electron densities $\sim 45\% >$ those corresponding to the Thomas-Fermi-Dirac atom are calc. The equations obtained are solved for a no. of ions and atoms, the Fermi-Amaldi correction term being used. The effect considered results in an increased attraction between atoms and ions. L. J. J.

Measurement of atomic radiating sources in crystals. II. Calculation of the absorption distribution for dipole radiation and determination of transition probabilities. K. H. Hellwege (*Z. Physik*, 1943, 121, 588–603; cf. A., 1944, I, 73).—The effect of at. dipole moment previously discussed is computed quantitatively for weak absorption. Absorption is dependent only on the orientation of the electric or magnetic vector. The inverse square root of the absorption const. taken in the corresponding direction gives an ellipsoid. The transition probabilities (oscillator strengths) can be determined as magnitudes independent of orientation, by one measurement for optically isotropic bodies, two for optically uniaxial crystals, and three for biaxial crystals. Of the two angles required to define the absorbing dipole, the measurements give neither, one, and both, respectively, in these cases. Data for hexagonal Nd Zn nitrate are given. L. J. J.

Theory of spherical waves excited at a finite distance from the plane separating two media for finite refractive index. M. Krüger (*Z. Physik*, 1943, 121, 377–437).—Mathematical. A. J. M.

Nuclear field theories. H. T. Flint (*Proc. Physical Soc.*, 1944, 56, 149–160).—A lecture survey covering the work of Fermi and others leading to Yukawa's deductions and theory. N. M. B.

Proper vibrations of a liquid drop and their application to nuclear physics. S. Flügge (*Ann. Physik*, 1941, [v], 39, 373–387).—Vibrations of a liquid drop for the general case of non-axially symmetric surface vibrations are calc. The rate of dissipation of such vibrational energy by radiation is calc. on the basis of classical electrodynamics and applied to the theory of nuclear isomerism.

Plane diffusion problems. G. C. Wick (*Z. Physik*, 1943, 121, 702–718).—An approx. method of solving plane diffusion problems is applied to problems of neutron physics. L. J. J.

Atomic radii from atomic and quantum numbers. S. T. Li (*J. Chinese Chem. Soc.*, 1943, 10, 169–172).—Equations, $r_1 = n^2/KZ$ or $n^3/(Z + 4)$ and $r_2 = n^2/hZ^{2/3}$, relating these quantities, are proposed. They give vals. in agreement with experiment. J. H. Ba.

II.—MOLECULAR STRUCTURE.

Application of the new analysis of molecular spectra to certain molecules. Simple explanation of certain molecular peculiarities. H. Deslandres (*Compt. rend.*, 1942, 215, 558–562).—A general survey and discussion of results of the author's later method of band-spectrum analysis. N. M. B.

Vibration spectrum of a crystal lattice.—See A., 1944, I, 143.

Band spectrum of silver hydride. L. Gero and R. Schmid (*Z. Physik*, 1943, 121, 459–487).—The band spectrum of AgH is reinvestigated, and the bands of the $\text{AgH}^+ \text{H}^-$ system are analysed. Vibrational term differences and rotation consts. of the lower state are calc. The homogeneous perturbation of the upper states is analysed. The term series of two mutually perturbing electronic states form a "network" in which the rotational terms with different vibration quantum nos. intertwine with each other. The analysis of the rotational and vibrational term differences in the upper states, the unusual intensity distribution in the bands, and the irregular isotope splitting of the band-lines can thus be explained. A. J. M.

Spectrum of nitric oxide: rotational analysis of ϵ bands and new observations on the β and δ band-systems. A. G. Gaydon (*Proc. Physical Soc.*, 1944, 56, 160–174).—Full data and a rotational analysis are tabulated for the (0, 4) and (0, 3) bands of the ϵ system of NO. Rotational consts. are evaluated; the upper electronic state is of type ${}^2\Sigma^+$. Potential-energy curves for the known electronic states of NO are shown. The excitation of the β and δ systems of NO in the N. afterglow is discussed. Bands of the β system with $v' = 5$ and 6 have been obtained in emission. The energy of dissociation of NO and supposed predissociation in the spectrum are considered. N. M. B.

Absorption of light in soap solutions. M. E. L. McBain (*J. Physical Chem.*, 1944, 48, 89–95).—Ultra-violet absorption by Na oleate solutions does not change regularly with concn., and duplicate measurements do not correspond. This effect is not due to light scattering but to the orientation of colloidal particles or lamellar micelles. C. R. H.

Relation of starch-iodine absorption spectra to the structure of starch and starch components.—Sec A., 1944, II, 188.

Effects of solvents on the absorption spectra of dyes. III Temperature and organic solutions of cyanine dyes. S. E. Sheppard and H. R. Brigham (*J. Amer. Chem. Soc.*, 1944, **66**, 380—384).—

Absorption spectra of 8 cyanine dyes in various solvents (EtOH, MeOH, Et₂O and C₆H₁₄) have been determined in the visible region at 90–300 K. Ionised dyes show no displacement of max. absorption. Bands are sharper at low temp., owing to suppression of rotation and low-order vibrational energies. Elimination of the auxiliary bands is not attained at 90° K. Sharpening of the bands first produces an increase in ϵ_{max} , followed by a decrease, which is less or absent in non-ionised dyes. Displacement of the spectrum of merocyanine dyes depends on the polarity of the solvent, indicating a coupling of dye and solvent mols. W. R. A.

Absorption spectra of the colouring matters of saffron. F. Poggio and M. Sanz Munoz (*Anal. Fis. Quim.*, 1942, **38**, 257—264).—Extinction curves for three fractions separated chromatographically from the Et₂O-insol. EtOH extract, and also for the total colouring matter, of Spanish saffron indicate the presence of picrocrocin. F. R. G.

Dependence of the intensity of fluorescence on the composition of a fluorescing solution. G. K. Rollefson and H. W. Dodgen (*J. Chem. Physics*, 1944, **12**, 107—111).—The relation between intensity (*I*) of fluorescence of solutions of fluorescein and acridone and the concn. of the fluorescer is expressed by a function which takes into account absorption of the exciting and fluorescent light and quenching by the fluorescer. At const. fluorescer concn. and in presence of KI as quencher the relation between *I* and [KI] is better expressed by Stern and Wolmer's than by Perrin's equation. This leads to the conclusion that quenching is a bimol. reaction competing with the unimol. reaction of fluorescence. C. R. H.

Luminescence spectra and vibrations in crystal lattices. D. D. Pant (*Proc. Indian Acad. Sci.*, 1943, **18**, A, 309—326).—A general survey of the luminescence spectra of crystals. Crystals giving discrete spectra are divided into seven classes, typified by diamond, Cr-activated luminescent solids, rare-earth phosphors, impurity-activated fluorescent solids, UO₂ compounds, solid C₆H₆, and solid N₂. Examination of the luminescence and absorption spectra of these solids suggests that vibrational ν are sharply monochromatic in all crystals. The spectra of some crystal constituents, e.g., N₂, C₆H₆ and UO₂, are similar to their gaseous spectra, but the observed bands are more discrete, owing to the absence of rotational es. W. R. A.

Action of added substances on the luminescence of lucigenin. I. K. Weber (*Z. physikal. Chem.*, 1941, **B**, 50, 100—115).—The action of added substances, which are usually inhibitors (KCl, KBr, KI, and KCNS) or catalysts (OsO₄, C₆H₅N, piperidine, and monohydric alcohols), on the fluorescence and chemiluminescence of NN'-dimethylacridylum nitrate (lucigenin) is investigated. Fluorescence is visible in neutral aq. solutions; chemiluminescence occurs when H₂O₂ is added to a strongly alkaline aq. solution. The inhibitors quench both forms of luminescence, so that either the initial intensity or both this and the total emission are reduced, as a result of action on either the exciting reaction or the excited mol. KI acts on the latter, KCl on the former, KBr and KCNS on both. Quinol possesses both a quenching and a catalytic effect. OsO₄, C₆H₅N, piperidine, MeOH, EtOH, Pr^oOH, Pr^oOH, Bu^oOH, and Bu^oOH show purely positive catalysis. The catalytic effect of the alcohols is \propto no. of C atoms in the chain. W. R. A.

Scope and limitations of infra-red measurements in chemistry. H. W. Thompson (*J.C.S.*, 1944, 183—192).—Tilden lecture. Points connected with the experimental technique of infra-red measurements are outlined. Vibrational absorption bands and their assignment to modes of vibration of the mol. are considered. The analysis of rotational structure of infra-red absorption bands also gives a method for assigning vibration frequencies, and for the determination of moments of inertia. Difficulties in the method due to perturbation of energy levels owing to interaction of vibration and rotation, and the fact that sufficient parameters cannot always be obtained to fix the structure, are emphasised. In the case of large or non-volatile mols, which do not show rotational contour, the vibration frequencies can be used to calculate useful thermodynamic properties. The allocation of a mol. to a symmetry class by using infra-red and Raman data together is considered. The application of infra-red spectroscopy to the investigation of the course of a reaction (e.g., addition to unsaturated compounds, condensation in the formation of high polymers, etc.) and the analysis of mixtures of related mols. (such as *o*-, *m*-, and *p*-isomerides, or *cis-trans* isomerides) is discussed. A. J. M.

Structure of the second CH harmonic and determination of integral extinction equivalents in the infra-red spectra of liquid aliphatic and aromatic hydrocarbons. R. Suhrmann and P. Klein (*Z. physikal. Chem.*, 1941, **B**, 50, 23—72).—The absorption spectra of 53 aliphatic, aromatic, and combined hydrocarbons and their derivatives are measured from 1.0 to 1.6 μ , with particular attention to the second

and the CH band at 1.4 μ . In standardising the spectrometer with H₂O, 5.9M-KI solution, and C₆H₆, a new H₂O band was found at 2.565 μ , together with several new C₆H₆ bands ρ_4 , mol. vol. and the wave nos., $\lambda\lambda$, and mol. extinction coeffs. of the principal bands are tabulated. In the presence of :CH₂, Me negative substituents, O bridges, and the CO group, the second harmonic separates into partial bands, the increase in aliphatic compounds with negative substituents occurring in the CH bonds of the C atom carrying the substituent. In aromatic compounds the more negative are the substituents, the greater is the increase in ν of the second CH harmonic. The presence of both aromatic and aliphatic CH bonds in the mol. produces two adjacent bands in the second CH harmonic. By measuring the area between the absorption curve and the ν axis, the internal extinction coeff. per CH bond, E_{CH} or E_{CH}^* in aliphatic or aromatic compounds, respectively, has been determined. Absorption in the second CH harmonic is the same in saturated hydrocarbons, in the alkyl halides (except EtI, Pr^oI and Bu^oI), in the ethers, and in NEt₃, but stronger in dioxan and cyclohexane, and weaker in nitriles, NO₂-compounds, and ketones. An aromatic CH bond absorbs more weakly in the second CH harmonic, and, although unaffected by one halogen atom, absorbs even less when several such atoms, or a CN or NO₂ group are present. Vals. of E_{CH} in aliphatic-aromatic compounds agree well with those calc. from E_{CH}^* and E_{CH}^* . Intensity of the second CH harmonic increases with decreasing mol. vol. It is suggested that the frequency drift on introducing a negative substituent may be determined by subtracting from the observed second CH harmonic the total absorption of the CH₂ and Me groups in the mol., vals. for the mol. extinction coeffs. of these partial bands having been derived from the spectra of the pure hydrocarbons. W. R. A.

Infra-red absorption of solid ammonium chloride and ammonium bromide. C. Beck (*J. Chem. Physics*, 1944, **12**, 71—78).—Infra-red absorption of solid NH₄Cl in the 7 μ . band shows no fine structure but a little very fine structure is given by NH₄Br. In the 5.6 μ . band both solids show at room temp. fine structure with similar spacing of the lines. NH₄Br shows also a still finer structure which cannot be resolved. At low temp. the fine structure of NH₄Br is decreased in intensity, and between -20° and -45° there is a change in the overall shape of the band. Fine structure persists down to 60°. Calculations show that the fine structure is due to rotation of the NH₄ group in the crystal and that this rotation continues, although altered, at temp. below the transition temp. of NH₄Br (-37.9°). C. R. H.

Raman spectra of crystals and their interpretation. R. S. Krishnan (*Proc. Indian Acad. Sci.*, 1943, **18**, A, 298—308).—Spectrograms of the Raman effect of NaCl crystals, obtained by Rasetti (A., 1931, 1352), are re-examined. Raman shifts, relative densities, and intensity ratios of Stokes to anti-Stokes lines are estimated for the 9 distinct lines on either side of the exciting ν . These ν are identified with harmonics of the forbidden fundamentals of the 9 normal modes of the NaCl lattice given by Raman's theory (A., 1944, I, 143). These observations cannot be explained by the Born theory of crystal dynamics. W. R. A.

Raman spectroscopy and its applications to glasses and glass-like synthetic materials. A. Simon (*Kolloid-Z.*, 1941, **96**, 169—186).—The Raman spectra of simple mols., mols. exerting intermol. forces, glasses, and high polymers are discussed with reference to structure. J. H.

Raman spectrum of vitamin-C and of its oxidation products. C. Bragnolo and Z. Ollano (*Gazzetta*, 1942, **72**, 571—577).—The Raman spectra of l-ascorbic acid (I) and of its first C-powder oxidation product (II) suggest that (I) is a furan derivative in which the olefinic form predominates over the "aromatic" resonance form, and that (II) has an open chain with a CO₂H group. E. W. W.

Dipole moments of friedelin, cerin, isomerides of friedelinol, and isomerides of α -chloro- γ -1-naphthyl- Δ^8 -propene. J. J. Lander and W. J. Svirbely (*J. Amer. Chem. Soc.*, 1944, **66**, 235—239).—Vals. of μ , calc. from dielectric const. (ϵ) measurements on C₃₀H₅₀ solutions of friedelin (I), high- (II) and low-m.p. friedelinol (III), cerin (IV), and the solid (V) and liquid (VI) forms of 1-C₁₀H₇-CH₂-CH₂-CHCl, are (I) 2.80 \pm 0.03, (II) 1.81 \pm 0.05, (III) 1.78 \pm 0.07, (IV) 2.39 \pm 0.05, (V) 1.27 \pm 0.02, and (VI) 1.47 \pm 0.02 d. Vals. of P_2 and μ do not depend on the abs. vals. of ϵ and ρ of the solvent. The error in P_2 , which arises from the relative errors in ϵ of the solvent, can be eliminated by using a val. of ϵ from the plot of ϵ against N_2 , extrapolated to $N_2 = 0$. Vals. of μ for (I)—(IV) support the postulated structures, whilst those for (V) and (VI) confirm the suggested *cis-(VI)-trans-(V)* isomerism. W. R. A.

New contributions to interferometry. III. Differential polarisation phase change on reflexion at a thin silver film. S. Tolansky (*Phil. Mag.*, 1944, [vii], **35**, 179—187).—The differential phase change for light polarised in and perpendicular to the plane of incidence on reflexion at a thin Ag film is measured for angles of incidence between 20° and 80°. To a first approximation the results confirm classical theory (MacLaurin, *Proc. Roy. Soc.*, 1906, **A**, 78,

296) but there is a small second-order discrepancy with a pronounced increase in the neighbourhood of 63° , which may be due to transition at the surfaces or to microcryst. structure in the film. The effect of the differential phase change in a high-resolution Fabry-Perot interferometer is discussed; it can only be important for plate separations $< \sim 1$ mm. H. J. W.

Size and form of ultramicroscopic particles. W. Hanke (*Z. Physik*, 1943, 121, 438—458).—Theoretical. Diffraction patterns formed by a double slit, the slits being narrow compared with their distance apart, are considered. A characteristic "visibility function," giving curves of equal visibility, is developed for various geometrical figures, and discussed. The function is applied to a parallelogram and a triangle. The results become particularly simple when the objects are smaller than the limit of resolution. The application of the characteristic function to diffraction at a double slit where the distance between the slits is of the same order as the slit width is also considered. A. J. M.

Relation between electronegativity and atomic number, quantum number, and valency. S. T. Li (*J. Chinese Chem. Soc.*, 1943, 10, 167—168).—The formula is given relating these quantities, $E = 2^{1/3}(z + 2.6)/km^2$, where $k = \text{const.} = 2.1$ when the quantum no. $n = 2$ and $= 2.3$ when $n = 3-6$, Z and z being at no. and valency. The calc. electronegativities of elements from Li to Bi agree with other determinations. J. H. B.

(A) Electronic resonance of 1-methyl-2-piperidone. (B) Energy of electronic resonance of 1-methyl-2-piperidone. P. S. Ugriumov (*J. Gen. Chem. Russ.*, 1943, 13, 217—221, 222—229).—(A) The dipole moment is shown by methods of analytical geometry to be 3.09×10^{-18} , whereas the experimental val. is 4.01×10^{-18} ; the difference is ascribed to resonance.

(B) The mol. heat of combustion is 882.4 kg.-cal., whereas the "calc." val. exceeds this val. by 24.0 kg.-cal. Similarly, the heat of formation from the gaseous elements exceeds that "calc." by 26.6 kg.-cal. The differences of 24.0 or 26.6 kg.-cal. represent the resonance energy. R. T.

cis-trans-Isomerism and cis-peak effect in the α -carotene set and in other stereoisomeric sets.—See A., 1944, II, 188.

Hydrogen content of white dwarf stars. G. Chertock (*Physical Rev.*, 1944, [ii], 65, 51—53).—Calculation of a mechanically stable model of the white dwarf Sirius B, considered as a completely degenerate gas, requires that the central core containing 11% of the mass and extending to 21% of the radius shall have no H_2 , and the remainder of the star shall have 45% H_2 . N. M. B.

III.—CRYSTAL STRUCTURE.

Precision determination of lattice constants by a compensation method. II. H. van Bergen (*Ann. Physik*, 1941, [v], 39, 553—572).—The lattice const. of calcite, rock-salt, Al, and Fe are determined by a compensation method due to Kossel (A., 1936, 925). The method, formerly used only for cubic crystals, is applied to hexagonal, tetragonal, and rhombic systems, and can be used for any type. The lattice const. for the above substances agree with those obtained by other methods. A. J. M.

Diffraction of X-rays by distorted-crystal aggregates. I. A. R. Stokes and A. J. C. Wilson (*Proc. Physical Soc.*, 1944, 56, 174—181).—Mathematical. The broadening of the Debye-Scherrer lines in X-ray photographs of cold-worked metals to be expected if due to distortion of comparatively large crystal grains is given by $\eta = \beta \cot \theta = 2/\phi_{hkl}(0)$, where β is the corr. integral breadth of the hkl reflexion, θ the Bragg angle, and $\phi_{hkl}(e)de$ the fraction of the crystal for which the tensile strain in the hkl direction is between e and $e + de$. Approx. relations of η with the internal stresses are given. N. M. B.

Definition of a crystal. G. Antonoff (*J. Physical Chem.*, 1944, 48, 95).—Objection is taken to the expression "isotropic crystals" for crystals having the same properties along the three main axes (e.g., NaCl), because the properties in other directions are not the same. Objection is also taken to referring to axes as being long or short and the term "intercepts" is proposed. C. R. H.

Crystal statistics. I. Two-dimensional model with an order-disorder transition. L. Onsager (*Physical Rev.*, 1944, [ii], 65, 117—149).—Mathematical. N. M. B.

Anisotropy of metals. H. S. Coleman and H. L. Yeagley (*Physical Rev.*, 1944, [ii], 65, 56—57).—Conclusions from available data are (1) that the anisotropy in the diffusion rate of one metal into another indicates that orientation may be the primary factor in controlling this rate, and (2) that there is an intimate relation between the crystal structure, plastic deformation, ferromagnetism, growth nucleation of metals, and intermetallic diffusion in the solid state. N. M. B.

Vibration spectrum of a crystal lattice. (Sir) C. V. Raman (*Proc. Indian Acad. Sci.*, 1943, 18, A, 237—250).—The normal modes of vibration of atoms in a crystal are derived from the most general

expression for the potential energy of displacement from the equilibrium position. In all possible modes, equiv. atoms have the same amplitude of vibration and either the same or alternately opposite phases in successive cells along each of the three axes of the lattice, thus forming a repeating space pattern, the "unit cell" of which has twice the dimensions of the lattice cell. The modes are closely analogous to those of a mol. with 8 times the no. of atoms in the lattice cell, and possessing the appropriate symmetry. The spectrum consists of a finite no. of discrete monochromatic ν , the no. of which is reduced in highly symmetric crystals. Degrees of freedom not included in this description appear as quasi-elastic vibrations of specifiable low ν . W. R. A.

Modes of atomic vibration in the fourteen Bravais lattices. G. N. Ramachandran (*Proc. Indian Acad. Sci.*, 1943, 18, A, 266—282).—Mathematical. The degeneracies and directions of the normal modes of vibration in the 14 Bravais lattices are derived by considering symmetry and using the theory of Raman (preceding abstract). Vibrations are of 8 types in the general case of no symmetry, but in partly symmetrical lattices some of the types and some directions of motion are equiv. The directions of motion and degeneracies of these types are found by selecting a group of symmetry operations, which results in coincidence of atoms in the same phase; directions of motion which satisfy the symmetry requirements of the group are then found. The no. of distinct modes for the $\Gamma_v, \Gamma_m, \Gamma_n, \Gamma_o, \Gamma'_v, \Gamma'_m, \Gamma'_n, \Gamma'_o, \Gamma_a, \Gamma_b, \Gamma_c, \Gamma'_a, \Gamma'_b, \Gamma'_c$ and Γ'' lattices are 21, 21, 15, 21, 15, 12, 12, 12, 8, 8, 8, 5, 4, 4. The modes are also described by considering symmetry only. W. R. A.

Normal oscillations of the diamond structure. S. Bhagavantam (*Proc. Indian Acad. Sci.*, 1943, 18, A, 251—256).—Mathematical. Group-theory methods are used to obtain the normal vibrations of the diamond structure, assuming a 16-atom cell as repeating unit. There are 8 normal vibrations, of which one is 3-fold, two are 4-fold, three are 6-fold, and two are 8-fold degenerate. The corresponding ν are derived by postulating suitable potential energy functions. W. R. A.

Frequency spectrum of the diamond lattice. E. V. Chelam (*Proc. Indian Acad. Sci.*, 1943, 18, A, 334—340).—Mathematical. Expressions for the ν of the eight normal modes of vibrations of the diamond lattice (cf. Chelam, *infra*) given by Raman's theory (*supra*) are derived, a suitable force field being used. W. R. A.

Frequency spectrum of crystalline solids. II. General theory and applications to simple cubic lattices. E. W. Montroll (*J. Chem. Physics*, 1944, 12, 111).—Errors are corr. (cf. A., 1944, I, 6). C. R. H.

Frequency spectrum of crystalline solids. III. Body-centred cubic lattices. E. W. Montroll and D. C. Peaslee (*J. Chem. Physics*, 1944, 12, 98—106).—The dynamics of a Born-Karman at. model have been developed on the assumption that the significant interactions are those between the nearest and next nearest at. neighbours, and that all internal vibrations are essentially harmonic. On the basis of this model the moments of the frequency spectrum, the relation between frequency spectrum and lattice const., and expressions for sp. heat have been deduced. C. R. H.

Normal vibrations in typical cubic crystals. E. V. Chelam (*Proc. Indian Acad. Sci.*, 1943, 18, A, 257—265).—The normal modes of vibration of simple, body-centred, and face-centred cubic lattices and of the lattices of ZnS, diamond, NaCl, CaF₂, and CsCl are derived, the theoretical methods of Raman (A., 1944, I, 143) being used. These lattices have 5, 4, 4, 9, 8, 9, 14, and 11 distinct ν . W. R. A.

Character tables for the atomic vibrations in cubic crystals. E. V. Chelam (*Proc. Indian Acad. Sci.*, 1943, 18, A, 327—333; cf. preceding abstract).—Mathematical. Character tables for groups associated with the vectors defining the normal modes are given for NaCl, diamond, ZnS, and CaF₂ lattices. The method of obtaining the normal modes from the tables is illustrated. W. R. A.

Normal vibrations of crystal lattices. Application of group theory. E. V. Chelam (*Proc. Indian Acad. Sci.*, 1943, 18, A, 283—297).—Group-theory methods, based on Raman's theory (A., 1944, I, 143), are used to derive the harmonic vibrations of a general crystal lattice. The rigorous derivation of the no. of normal modes, and their ν and degeneracies, is described. W. R. A.

Modes of vibration of the hexagonal close-packed lattice. G. N. Ramachandran (*Proc. Indian Acad. Sci.*, 1943, 18, A, 341—344).—Mathematical. The modes of vibration of the hexagonal close-packed lattice are derived by Chelam's method (cf. *supra*) based on Raman's theory of crystal vibrations (A., 1944, I, 143). Character tables are constructed. There are 13 distinct modes, of which one is non-degenerate, two are 2-fold, six are 3-fold, one is 4-fold, and three are 6-fold degenerate. The crystal planes involved, and the direction of vibration of each mode, are described. W. R. A.

State of order in felled and netted structures caused by mechanical deformation, especially in the case of polystyrene. F. H. Muller (*Kolloid-Z.*, 1941, 96, 326—332).—A review (cf. A., 1944, I, 29). J. H. B.

Molecular structure of liquids. H. A. Stuart (*Kolloid-Z.*, 1941, 96, 149—160).—The structure of liquids consisting of mols. of various shapes and charge distributions is discussed on the basis of the results of experiments with models (cf. A., 1938, I, 123). Physical properties are correlated with the structures obtained.

J. H. BA.

Chemical morphology of liquids. III. Liquid-crystalline aliphatic monocarboxylic acids.—See A., 1944, II, 179.

Structure of water. F. I. Havlicek (*Z. Physik*, 1943, 121, 495—500).—Starting from the crystal structure of ice given by Bragg, Barnes, and Bernal and Fowler, and Debye's model of the H_2O mol., a model for the association of H_2O is drawn up, a hexagon being the fundamental structural element. The binding energy is discussed.

A. J. M.

Structure relationships between salts and amorphous hydroxides of trivalent metals. H. W. Kohlschütter (*Kolloid-Z.*, 1941, 96, 237—244).—A review of the experiments on the formation of the hydroxides of Fe^{+++} , Cr^{+++} , and Al^{+++} from neutral and basic salts in the solid state and in solution. The structures and properties of the hydroxides formed are determined in part by those of the salts from which they are prepared.

J. H. BA.

Electron-microscopic and X-ray investigation of the structure of soots. M. von Ardenne and U. Hofmann (*Z. physikal. Chem.*, 1941, B, 50, 1—12).—The particle sizes of three soots, (I) from a C_2H_2 flame, (II) from the explosive decomp. of C_2H_2 , and (III) from the action of finely-divided Fe on CO at 700° , are determined by X-ray analysis and with the electron microscope. Surface area per g. was determined by colorimetric estimation of the adsorption of methylene-blue. The soot was prepared for electron-microscopic examination by evaporation of a xylene suspension on a vibrating slide. Particle diameters are (I) 25, —; (II) 200, 200—300; (III) 400, 100—500 Å., the first val. being that from X-ray analysis. Surface area, calc. from particle size, differs markedly in (I), but less in (II) and (III), from that determined by adsorption. These deviations are explained by the fact that electron-micrographs show that (I) consists of dense aggregate particles, and that in (II) and (III) aggregation is much less compact.

W. R. A.

Structure of micro-crystalline carbon. U. Hofmann, A. Ragoss, and F. Sinkel (*Kolloid-Z.*, 1941, 96, 231—236).—Differences in activity between various types of C are attributed to various crystal sizes and their packing. X-Ray comparison of C_2H_2 soot (I), retort-scale C, and coke show that graphitisation occurs the more readily the more dense is the original structure. The structures of (I), gas (II), and flame soots (III) are examined by methylene-blue adsorption, X-rays, and electron microscope, before and after graphitisation. The ratio of the surface area, as determined by X-rays and adsorption, gives a measure of the close packing of the crystals, and is found to increase in the order (III) > (II) > (I). Electron micrographs confirm that on graphitisation the tendency to recrystallise to bigger crystals is also in this order.

J. H. BA.

Crystal structure of potassium silver carbonate, $KAgCO_3$. J. Donohue and L. Helmholz (*J. Amer. Chem. Soc.*, 1944, 66, 295—298).—The crystal of $KAgCO_3$ is orthorhombic holohedral, a_0 20.23, b_0 5.75, c_0 5.95 Å., space-group D_{2h}^{14} —*Ibca*. The Ag—O distance, 2.42 Å., is discussed in relation to other Ag salts, including Ag_2CO_3 , for which preliminary data are: a_0 4.83, b_0 9.52, c_0 3.23 Å., β 92.7° , z 2, probable space-group C_{2h}^2 — $P2_1$. The application of the rule of Pitzer *et al.* (A., 1941, I, 451) to the probable nature of the Ag—O bond is discussed.

W. R. A.

Constitution of the aluminium-vanadium compound, VAL_3 . G. Brauer (*Z. Elektrochem.*, 1943, 49, 208—210).—Interaction of V_2O_5 , pure Al, and Na_3AlF_6 in an atm. of A, followed by slow cooling of the product from 1200° to 500° , yields the compound VAL_3 , which can be separated from the excess of Al by utilising its less rapid dissolution in HCl or aqua regia and finally by centrifuging in MeI + Et_2O mixture (d 3.2). Like $TiAl_3$ it crystallises in a tetragonal quadratic form, space-group D_{4h}^{18} , with a 5.334 and c 8.305 Å.; d 3.68 from X-ray data, and 3.34 pyknometrically.

J. W. S.

Active substances. XLIX. X-Ray and electron-microscopic investigation of the thermal transformation $\gamma\text{-FeOOH} \rightarrow \gamma\text{-Fe}_2O_3 \rightarrow \alpha\text{-Fe}_2O_3$. R. Fricke, T. Schoon, and W. Schröder (*Z. physikal. Chem.*, 1941, B, 50, 13—22).—Changes in particle and crystal structure in the series $\gamma\text{-FeOOH} \rightarrow \gamma\text{-Fe}_2O_3 \rightarrow \alpha\text{-Fe}_2O_3$ are investigated by X-ray diffraction and with the electron microscope. The large differences in dimensions of the crystals, calc. from the X-ray diffraction diagrams, and of the particles visible in the electron microscope, show that the latter are secondary aggregates. The shape and size of these secondary aggregates remain almost unchanged up to the transformation into $\alpha\text{-Fe}_2O_3$ at 500° , whereas the size of the primary particles of FeOOH increases on heating, but decreases considerably in the transformation into $\gamma\text{-Fe}_2O_3$, finally increasing, with the formation of plate-shaped crystals. In the transformation into $\alpha\text{-Fe}_2O_3$, heating to 750° is necessary before the needles, visible in the electron microscope, are replaced by dense secondary aggregates.

W. R. A.

Crystal structure of copper *N,N*-di-*n*-propyldithiocarbamate. I. G. Peyronel (*Gazzetta*, 1943, 73, 89—94).—The crystal structure of this compound (cf. Malatesta, A., 1938, I, 128) is studied goniometrically and by X-ray (rotating crystal and Weissenberg) methods. It belongs to the $2_1 \times 2/m$ prismatic class of the monoclinic system, with lattice consts. a 13.25, b 18.60, c 8.27 Å.; 90° 48'; 4 mols. per unit cell. The symmetry group is C_{2h}^2 or C_{2h}^1 . Cu occupies a centre of symmetry with planar co-ordination.

E. W. W.

Structure of the "B" modification of starch from film and fibre diffraction diagrams. R. E. Rundle, L. Daasch, and D. French (*J. Amer. Chem. Soc.*, 1944, 66, 130—134; cf. A., 1941, I, 451).—Films were prepared from solutions of amylose (I) and used, after stretching, for X-ray examination. The specimens, in contrast with whole starch, contain no branched chains, the mols. being linear aggregates of ~200 glucose residues. The unit cell has a_0 16.0, b_0 10.6, c_0 9.2 Å., and is probably orthorhombic. Calc. d of crystal portion 1.6. The structure proposed is based on the space-group D_{2h}^1 , although D_{2h}^2 is equally likely. Fibres were also prepared, but are difficult to stretch sufficiently to produce good orientation. The configuration of (I), unlike that of cellulose, depends on its treatment. In "B" the chains are fully extended, in "V" and in the I-complex they are helical, and when treated with certain plasticisers they assume an intermediate crumpled form.

F. L. U.

Micellar structure of cellulose. O. Kratky (*Kolloid-Z.*, 1941, 96, 301—310).—The state of dispersion of cellulose in xanthate solutions is considered, and X-ray pictures of cellulose pptd. from such solutions and in various degrees of extension and swelling are shown to agree quantitatively with a structure consisting of plate micelles joined by thread mols.

J. H. BA.

Microscopic and electron-microscopic investigations on macromolecular substances. (Frl.) M. Staudinger (*Chem.-Ztg.*, 1943, 67, 316—320).—The study of synthetic polymers of known structure, e.g., polyoxymethylenes and polyethylene oxides, as a preliminary to investigation of natural polymers, e.g., cellulose, is discussed. With linear macromol. substances the capacity for fibre formation runs parallel with the chain length. Photomicrographs are shown of polyoxymethylene crystals degraded by acids and alkalis. Cellulose fibrils are more stable towards chemical degradation, but its effect becomes apparent after swelling or mechanical treatment. Bacterially degraded fibres are attacked only locally, and the average degree of polymerisation is not much reduced. The possible arrangements of macromols. in the cell-wall are considered.

R. H. F.

The ultrasonic diffraction grating. R. A. Houstoun (*Phil. Mag.*, 1944, [vii], 35, 192—202).—Stationary ultrasonic waves produced by a quartz plate in a periodic electric field are accompanied by a harmonic variation in n ; the plate can then act as a diffraction grating. Experiments with various quartzes and oscillators are described. The quartz grating can be used for measuring the velocity of light by reflecting the diffracted beam back through the quartz after traversing a path of known length (~4 m. in H_2O). The quartz can also be used as a wave-meter since the grating effect depends on resonance between the applied field and the natural frequencies of the quartz. An arrangement for determining the persistence of luminosity in an electrodeless discharge in a gas at low pressure is also suggested; no positive results have so far been obtained.

H. J. W.

Loss of colour of alkali halide crystals. H. Kurzke and J. Rottgardt (*Ann. Physik*, 1941, [v], 39, 619—632).—Moisture may cause bleaching of a coloured alkali halide crystal. The mechanism of the process is discussed.

A. J. M.

Flow of polycrystalline metals. U. Dehlinger and A. Kochendorfer (*Z. Elektrochem.*, 1943, 49, 228—233).—The plastic deformation of single crystals is discussed and compared with flow in fluids. For a crystal deranged by rapidly varied stress, as with a crystal containing occluded foreign atoms, the crit. deformation resistance is greatly increased. With metals containing crystals of varying orientation the elastic limit is reached when the stress equals the mean val. of the elastic limits of the individual crystals. The special stresses arising near the crystal interfaces are discussed. The theory developed leads to the inference that the elastic limits of soft Al and Cu should vary little with varying temp., whereas that of Fe should be very temp.-dependent. This has been confirmed experimentally.

J. W. S.

Cross-section contraction number [Poisson's ratio] in the periodic system. W. Koster (*Z. Elektrochem.*, 1943, 49, 233—237).—Poisson's ratio (μ) for metals, calc. from the ratio of the moduli of compression and elasticity, is a periodic function of the at. no., metals of the same group having closely similar vals. The μ vals. calc. from the c_{12} and c_{44} elasticity consts. of single crystals are in closer accord with the vals. obtained from polycryst. samples the lower is the elastic anisotropy of the metal.

J. W. S.

Structure of fritted powders. G. F. Hüttig (*Kolloid-Z.*, 1941, 96, 227—230).—The process of fritting is defined as the joining of powder particles without the formation of a liquid phase. The vol. occupied by capillaries (1.5 — 5.5×10^{-7} cm. diameter) in powdered Cu on raising the temp. to 600° shows two max. at $\alpha = 0.35$ and

$\alpha = 0.48$, where $\alpha = (\text{abs. temp.})/(\text{abs. m.p.})$. Similar max. at approx. the same vals. of α are observed for Fe, Fe_2O_3 , $\alpha\text{-Al}_2\text{O}_3$, and BeO . The first max. is concerned with the surfaces only, but the second involves the crystal lattice. J. H. B.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Physical data of Δ^o -olefines and n -paraffins.—See A., 1944, II, 177.

Physical data of $\alpha\alpha$ -diphenyl-alkenes and -alkanes and $\alpha\omega\omega$ -tetraphenylalkenes.—See A., 1944, II, 189.

Approximate method for the calculation of magnetic susceptibility. H. Koppe (*Z. Physik*, 1943, 121, 614—628).—Susceptibility calculations are based on the eigenfunctions of H in a magnetic field, taking into account perturbations due to coulombian interaction of electrons. L. J. J.

Magnetic properties of non-homogeneous systems. L. F. Bates and E. M. Somckh (*Proc. Physical Soc.*, 1944, 56, 182—194).—The magnetic susceptibilities of dil. amalgams of 12 metals were measured by a new method using cylindrical pole surfaces shaped in accordance with recent theoretical work. Results tabulated and discussed show that all these metals are paramagnetic in dil. solution in Hg to an extent which is usually compatible with an increase in the no. of free electrons in the amalgam. N. M. B.

Absolute diamagnetism of superconductors. K. M. Koch (*Z. Physik*, 1943, 121, 488—494).—A reply to criticism by Neugebauer (A., 1943, I, 222). A. J. M.

Damping of mechanical oscillations by magnetic hysteresis. M. Kornetzki (*Z. Physik*, 1943, 121, 560—573).—Changes in magnetisation caused by uniform mechanical strain in the Weiss regions show a residual effect after removal of the applied stress. Hence there is a dissipation of energy during mechanical oscillation. The resulting damping increases with amplitude of vibration, and \propto the Rayleigh hysteresis const. and \propto the third power of the ratio of saturation magnetostriction to saturation magnetisation. I. J. J.

Collision excitation of intramolecular vibration in gases and gaseous mixtures. VIII. Ease of excitation of various normal vibrations from measurements of the dispersion of sound. K. F. Buschmann and K. Schafer (*Z. physikal. Chem.*, 1941, B, 50, 73—99).—The dispersion of sound in CO_2 , NH_3 , N_2O , and Me_2O is measured at normal temp., and relaxation times are calc. A dependence of relaxation time on the pressure of the gas and ν of the sound could be recognised. This dependence shows that vibrations requiring a collision from a direction perpendicular to the mol. axis for their excitation are less easily excited than those requiring a collision in the direction of the mol. axis, in agreement with results obtained from exchange reactions. Deviations, observed only in N_2O , appear to arise from the tendency of this gas to thermal decomp., although a rigid explanation cannot be advanced. W. R. A.

Refractive indices of the normal saturated aliphatic nitriles. A. Dorinson and A. W. Ralston (*J. Amer. Chem. Soc.*, 1944, 66, 361—362).—Vals. of n_D^{20} ($\theta = 20^\circ$ — 75°) are given for normal aliphatic nitriles from butyrol to stearyl-nitrile; for each compound, an abrupt change in slope in n - θ curves is exhibited at ~ 40 — 45° . W. R. A.

Specific heats at low temperatures of calcium sulphite, sodium sulphite, and manganese dithionate dihydrate. K. K. Kelley and G. E. Moore (*J. Amer. Chem. Soc.*, 1944, 66, 293—295).—Vals. of C_p from 53° to 295° K. have been determined for CaSO_3 , Na_2SO_3 , and $\text{MnS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, giving vals. of entropy at 298.16° K. of 24.2 ± 0.3 , 34.9 ± 0.4 , and 66.7 ± 1.0 g.-cal. per degree per g.-mol. There appears to be a difference in entropy between a sulphate and a sulphite group in a solid of ~ 1 g.-cal. per degree per g.-mol. at 298.16° K. W. R. A.

Heat capacity, heats of transition and vaporisation, vapour pressure, and entropy of $\alpha\alpha\alpha$ -trichloroethane. T. R. Rubin, B. H. Levedahl, and D. M. Yost (*J. Amer. Chem. Soc.*, 1944, 66, 279—282).— C_p for CMeCl_3 has been measured at 14 — 300° K. At 224.20° there is a transition point with heat of transition 1786 ± 2 g.-cal. per g.-mol. M.p. $\sim 240.2 \pm 0.5^\circ$ K., heat of fusion $\sim 450 \pm 300$ g.-cal. per g.-mol. From 268° to 290° K. the v.p. equation is $\log p = -(1729/T) + 6.92013$. Heat of vaporisation at 286.53° K. is 7962 ± 12 g.-cal. per g.-mol. Entropy vals. are: gas at 286.53° K., 76.22 ± 0.16 , and at 298.16° K., 76.97 ± 0.16 ; liquid at 298.16° K., 54.37 ± 0.12 g.-cal. per degree per g.-mol. From spectroscopic data, on the assumption of free rotation, $S_{298.16}^{298.16}$ (1 atm.) is 77.47 ± 0.10 g.-cal. per degree per g.-mol., corresponding with a barrier of 2700 ± 350 g.-cal. per g.-mol. W. R. A.

Densities of liquids and their temperature changes. G. Antonoff (*J. Physical Chem.*, 1944, 48, 80—85).—The thermal history of a liquid influences its d ; bringing the liquid to a given temp. does not necessarily give the same val. of d . Accurate d data for Pr°OH , obtained over the range 25 — 85° , show that there is a kink in the d curve at $\sim 60^\circ$, and that the d of freshly purified Pr°OH is $< d$ of

aged specimens. Intramol. tautomerism, intermol. reaction, and polymerisation are suggested as reasons for the observed effects. C. R. H.

Densities and transition points of normal paraffin hydrocarbons. W. F. Seyer, R. F. Patterson, and J. L. Keays (*J. Amer. Chem. Soc.*, 1944, 66, 179—182).—Measurements of ρ for even-numbered paraffin hydrocarbons (C_{18} to C_{34}) show that, for each, the structure in the liquid and solid states is identical. The C_{29} homologue has a solid phase much less dense than even-numbered neighbours. The transition points of hydrocarbons C_{24} to C_{34} can be observed with either heating or cooling, whilst for C_{18} to C_{20} the transition point is observed only on cooling. W. R. A.

Vapour pressure of beryllium at 1170 — 1340° K. R. Schuman and A. B. Garrett (*J. Amer. Chem. Soc.*, 1944, 66, 442—444).—Vals. of the v.p. of Be between 1170° and 1340° K., determined by the Langmuir method, are given. The mean val. of ΔH_0° is $122,000 \pm 2500$ g.-cal. per g.-mol. The calc. heat of vaporisation at 1250° K. is $78,800$ g.-cal. per g.-mol. The accommodation coeff. appears to be 1. W. R. A.

Regularity of vapour pressures of organic substances belonging to homologous series. A. Giacalone (*Gazzetta*, 1942, 72, 370—377).—In aliphatic series, the ratio (R) of the v.p., at const. temp., of any member to that of the one next above is approx. const. (at 20° , ~ 2.5 — 3.5), and differs little from series to series; it decreases with temp. The decrease in molar free energy, calc. from R , for each additional CH_2 group in the hydrocarbon series ~ 710 g.-cal. (cf. Parks *et al.*, A. 1930, 877). There is an approx. const. difference in the temp. at which two successive homologous members have the same v.p. E. W. W.

Vapour pressure and heat of vaporisation of trichloroethylene. H. J. McDonald (*J. Physical Chem.*, 1944, 48, 47—50).—Over the range 18 — 86° the v.p. of C_2HCl_3 is represented by $\log p = 30.482609 - 2936.227/T - 7.999975 \log T$, where $T = \text{abs. temp.}$. At the b.p. and at 1 atm. the heat of vaporisation is 7679 ± 100 g.-cal. per g.-mol. Over the range 0 — 60° C_2HCl_3 has $d_4^{20} = -0.0016180 + 1.4980$, and over the range 17 — 27° $n_D = -0.0005765\theta + 1.4890$, where $\theta = \text{temp. in } ^\circ\text{C.}$ C. R. H.

Thermal expansivity and density of indium. P. Hidnert and (Miss) M. G. Blair (*J. Res. Nat. Bur. Stand.*, 1943, 30, 427—433).—The linear thermal expansion of high-purity cast In is investigated at 20 — 100° by the precision micrometric thermal expansion apparatus of Souder and Hidnert (B., 1926, 789) and at -190° to 0° by the fused-quartz tube thermal expansion apparatus of Hidnert and Sweeney (B., 1928, 930). Within the range -190° to 100° , the linear expansion of In is expressed by the equation: $L_\theta = L_0[1 + (28.9\theta + 0.013\theta^2) \times 10^{-6}]$, where L_0 and L_θ are the lengths of the metal at 0° and θ° . The average coeffs. of cubical expansion of In are 77×10^{-6} (0 — 25°) and 101×10^{-6} (25 — 50°). These are not three times the corresponding coeffs. of linear expansion because of the anisotropy of In. The d of cast In, calc. from the best data on at. wt. and lattice consts., is 7.40 , within 2% of the observed val. of 7.281 for $d^{22.6}$. J. F. H.

Supplementary postulates and the gas law. R. W. Pohl (*Z. Physik*, 1943, 121, 543—545).—Examples of confusion arising from neglect of certain assumptions in the formulation of fundamental laws are given. L. J. J.

Equation of state for saturated fluids. J. E. Haggengmacher (*J. Amer. Chem. Soc.*, 1944, 66, 313).—The expression, $p = CT/(v_s + v_l + 2B)$, where $C = R/M$, $B = (CT_c/2P_c) - v_c$ (p = saturation pressure; T = saturation temp. in $^\circ\text{K.}$; v_s , v_l = sp. vols. of saturated vapour and saturated liquid; M = mol. wt.; T_c , P_c , v_c = crit. temp., pressure, and vol.), has been derived from a more general, three-const. quadratic equation of state for saturated fluids. Of the 59 substances tested with this expression, only AcOH shows anomalous behaviour, which may be explained by association. Agreement with observation is best for the simple gases, e.g., He, H₂, Ne, N₂. W. R. A.

Relation between liquid and gaseous states of metals. L. Landau and J. Zeldovitch (*Acta Physicochim. U.R.S.S.*, 1943, 18, 194—196).—The existence of a continuous spectrum of electron energy levels is necessary but not sufficient for the metallic state; to ensure conductivity it must be possible for charge to be transferred between the fundamental state and adjacent excited levels. In dielectrics there is a finite gap at all temp. between such levels, continuous transition to metallic conduction being impossible except at $\sim 10^4$ K. Three cases are distinguished for metal-gas transition: (i) a single crit. point at very high temp., (ii) a liquid-gas crit. point at a temp. \ll that of the crit. metal-dielectric point (e.g., Hg), with the co-existence of two metallic and one dielectric phases, or (iii) one metallic and two dielectric (liquid and gaseous) phases. For Hg there are predicted a non-conducting liquid phase and a phase transition above the normal crit. point with a discontinuous change of electrical conductivity, sp. vol., and other properties. L. J. J.

Determination of critical temperature from b.p. M. C. Chen and D. B. Hu (*J. Chinese Chem. Soc.*, 1943, 10, 212—215).—The expres-

sion $T_c = 10^{1.59/\sqrt{M}} T_B$ gives good agreement with observed vals. of T_c for a large no. of compounds. J. H. Ba.

Additive function of mol. wt. and critical temperature. D. B. Hu and M. C. Chen (*J. Chinese Chem. Soc.*, 1943, 10, 208—211).—The expression $M \log_{10} T_c + 6.41/\sqrt{M}$ is shown to be additive for a large no. of compounds (cf. Burnop, A., 1938, I, 393).

Viscosity of compressed gases. O. Leipunski (*Acta Physicochim. U.R.S.S.*, 1943, 18, 172—182).—According to available published data, Enskog's formula describes accurately the viscosity of pure gases up to ~ 1000 atm. for N_2 , H_2 , CO_2 at 100°, and CO , and up to 300 atm. for H_2O at 370°, 600 atm. for CH_4 at 25°, 30 atm. for NH_3 at 80°, and 150 atm. for O_2 at 50°. The formula describes the change of η of gas mixtures with pressure with fair accuracy if the const. b is taken as the mean of vals. for the components.

Hydrogen bond. J. N. Friend (*Chem. and Ind.*, 1944, 179).—Investigation of η of a no. of org. compounds from room temp. to the b.p. agrees with the view that there is a close connexion between η and the H bond. Replacement of OH in PhOH by OMe markedly reduces η in spite of the increase of mol. wt. Replacement of Me by heavier alkyl groups causes increase of η . Similarly the η of NH_2Ph is progressively reduced by successive replacement of the H of NH_2 by Me, but the η of $NPhMe$ is increased by substituting Me by heavier alkyl groups. Extrapolation indicates that the η of $NPhBu_2$ will probably be approx. the same as that of $NHPh$.

Viscosities of di- and tri-methylamine at 15°, 25°, and 35°. E. Swift, jun., and D. L. Wolfe (*J. Amer. Chem. Soc.*, 1944, 66, 498—499).—Experimentally determined vals. of η at 15°, 25°, and 35° (reliable to only 1%) are: for $NHMe$, 2.07, 1.86, and 1.67, and for NMe_3 , 1.94, 1.77, and 1.61 m-poise.

Kinetic theory of thermo-diffusion in liquids. K. Wirtz and J. W. Hiby (*Physikal. Z.*, 1943, 44, 369—382).—Thermal diffusion in liquids is considered, using a quasi-cryst. model for the place-exchange process. Isothermal migrational processes (diffusion and ionic mobility) are discussed on the basis of the model. The activation energy for place exchange is divided arbitrarily into two parts, one the energy necessary to bring the particle into the position of rest before the change, and the other the energy the particle has in the new position of rest; the latter depends on the size of the particle. These two portions of the energy influence the Soret effect in opposite directions. The movement of a stream of particles in a temp. gradient is considered on this basis, and an expression for the Soret coeffs. is obtained. The work is extended to dil. solutions of electrolytes, giving diffusion potentials. The laws obtained agree with those deduced by Wagner on thermodynamic grounds. The anomalous behaviour of the Soret effect in alkalis is related to anomalies of mobility. The theory explains why the heavier mols. of a liquid mixture migrate towards the warm wall in thermo-diffusion. The isotope effect of the Soret coeffs. is discussed, and it is shown that it is the size of the isotope mol. which is responsible for separation.

Thermodynamics of thermal diffusion. J. Meixner (*Ann. Physik*, 1941, [v], 39, 333—356).—Irreversible processes, e.g., diffusion, can be approached by "thermodynamic-phenomenological" methods, taking into account (i) material, energy, and impulse conservation principles and a spatial distribution of entropy sources, but no entropy sinks, (ii) experimental laws relating rates of irreversible processes with the appropriate potential factors, and the Onsager reciprocity law. These methods are applied to thermal conduction in anisotropic crystals, thermo-diffusion with convection in a binary ideal gas mixture, and thermo-diffusion in paramagnetic gases. The theory is in harmony with Eastman and Wagner's transfer-heat concept.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Demonstration experiment on emanation diffusion. A. Krebs (*Ann. Physik*, 1941, [v], 39, 330—332).—The diffusion of radioactive emanation through different gases is followed by observations of the progress and intensity of fluorescence on a phosphor film supported on a glass strip or tube in a glass tube to one end of which the emanation is admitted.

Diffusion of inert gases through metals. W. Lumpe and R. Seeliger (*Z. Physik*, 1943, 121, 546—559).—Inert gas occluded in metals becomes appreciably mobile at $\sim 100^\circ$ and its mobility increases markedly with temp.

Diffusion thermo-effect. L. Waldmann (*Z. Physik*, 1943, 121, 501—522).—The kinetics of thermo-diffusion are derived from the Boltzmann equation. The material and thermal flux of diffusion are proportional to the same coeff., the "thermodiffusion factor" (α). Temp. distribution in diffusion chambers with adiabatic walls is calc. Diffusion of N_2 into H_2 can give temp. differences up to 7° , and diffusion of ^{22}Ne into ^{20}Ne can give 0.8° . The coeff. α can be

calc. from the observed temp.-time integral. An application of the effect to gas analysis is suggested. L. J. J.

Thermodynamics of thermal diffusion.—See A., 1944, I, 149.

Determination of mol. wt. of organic substances by dialysis. (A) H. Brintzinger. (B) H. Spandau (*Ber.*, 1941, 74, [B], 1025—1028, 1028—1030).—(A) The method of Spandau and Gross (A., 1943, I, 304) is invalid because of variation of K for different org. substances, even for isomerides; mol. shape is an over-riding factor. A difficulty of technique is noted.

(B) K vals. are const. (23 examples) if wide-pored membranes are used. The difficulty of technique is overcome. R. S. C.

Mixture law for viscosity. F. Kottler (*J. Physical Chem.*, 1944, 48, 76—80).—Derivations are given for the fluidity equations for ideal and non-ideal mixtures previously reported (cf. A., 1943, I, 224). The conditions which must be fulfilled in obtaining the data so as to test the equations are laid down. The use of mol. fractions and not wt. or vol. fractions is imperative. C. R. H.

Pyrazine-water azeotrope. H. F. Pfann (*J. Amer. Chem. Soc.*, 1944, 66, 155).—Pyrazine and H_2O form a min.-boiling 60:40 azeotrope, b.p. 95.5° . R. S. C.

Influence of electrolytes on the rotatory power of *d*-tartaric acid. L. Yang and P. F. Hu (*J. Chinese Chem. Soc.*, 1943, 10, 184—189).—HCl causes an initial sharp fall in the rotation followed by a gradual decrease at higher concns. Addition of NaOH shows a max. and NaCl is similar to HCl at the higher concns. The observations are accounted for in terms of the effect of the additions on the ionisation of tartaric acid and an electrolyte effect. J. H. Ba.

Entropy change during alloy formation.—See A., 1944, I, 155.

Diffusion of copper, magnesium, manganese, and silicon in aluminium. H. Buckle (*Z. Elektrochem.*, 1943, 49, 238—242).—The diffusion consts. (D) of Cu, Mg, Mn, and Si in Al have been determined at 400 — 600° . In each case D decreases with increasing concn. of alloying element. The energies of dissolution are evaluated.

Solubility in aluminium of Mg, Si, Mg, Ge, Mg, Sn, and Mg, Pb. H. Westlinning and W. Klemm (*Z. Elektrochem.*, 1943, 49, 198—200).—At 500° the solubilities in Al of Mg, Si, Mg, Ge, Mg, Sn, and Mg, Pb, as determined by X-ray and microscopical examination of quenched samples, are ~ 0.4 , 0.2 , 1.8 , and 0.2 mol.-%, respectively. These vals. show a decrease with increasing polarisability of the anion. The solubilities of Mg_2Sn and Mg_2Ge decrease with decreasing temp. much more rapidly than that of Mg_2Si . J. W. S.

Surface treatment of metallic surfaces by diffusion. H. Vosskuhler (*Z. Elektrochem.*, 1943, 49, 204—208).—Heating of Al-Li alloy (6.69% Li) in air or in a $Na_2Cr_2O_7$ - $K_2Cr_2O_7$ bath at 590° , Mg-Ca alloy (1.98% Ca) in air at 500° , or Al-Mg alloy ($\sim 8.5\%$ Mg) in a $NaNO_3$ - KNO_3 bath at $\sim 400^\circ$ decreases the surface concn. of Li, Ca, and Mg, respectively. In each case a homogeneous layer is formed over the heterogeneous material and the metal becomes less corrodible.

Solubility of MgZn, in aluminium. G. Siebel (*Z. Elektrochem.*, 1943, 49, 218—220).—X-Ray and microscopic investigations indicate that the solubility of MgZn in Al increases from 1.4 wt.-% at 150° to ~ 17 wt.-% at 475° . The results are in accord with previous data for temp. $> 325^\circ$ but are $<$ previous vals. for higher temp.

Magnetic investigation of a nickel-carbon alloy. W. Gerlach and J. von Rennenkampff (*Z. Elektrochem.*, 1943, 49, 200—203).—The anomalous temp.-variation of the magnetisation of Ni saturated with C by fusion in a C crucible is explained by assuming that the cooled sample is a mixture of alloys of varying C content in which that with Curie point $\sim 50^\circ$ predominates. Reheating causes pptn. of C and hardening of the metal. J. W. S.

Structures of metalloid alloys and ferromagnetism. H. Nowotny (*Z. Elektrochem.*, 1943, 49, 254—260).—The binary systems of Cr, Mn, Fe, Co, and Ni with N, P, As, Sb, and Bi are closely analogous in that several compounds of the types MX , M_2X , M_3X , and M_4X are formed. These are regarded as interstitial compounds. Such compounds of Cr and Mn are often ferromagnetic, this behaviour being discussed theoretically. J. W. S.

Magnetic properties [of dilute amalgams].—See A., 1944, I, 147.

Line co-ordinate representation of solubility curves. F. E. E. Germann and R. P. Germann (*Ind. Eng. Chem.*, 1944, 36, 93—96).—On the basis of Mortimer's solubility equation, $-\log X = 0.05223a/T + b$, where X = mol. fraction of solute in solution at temp. T and a and b are consts., a chart, which enables the solubility of a solute in a given solvent over a range of T to be obtained, has been constructed. The chart is applicable to 17 org. solutes with several org. solvents for each solute, 131 two-component systems being represented.

C. R. H.

Thermochemistry of chlorine monoxide [solubility in water].—See A., 1944, I, 155.

Solubility of sodium iodide in aqueous sodium hydroxide at 20° . R. Pomeroy and H. D. Kirschman (*J. Amer. Chem. Soc.*, 1944, 66,

178—179).—The solubility and ρ of NaI in aq. NaOH (0—15.2N.) have been determined. A discontinuity, representing the transition $\text{NaI} \cdot 2\text{H}_2\text{O} \rightarrow \text{NaI}$, has been found with a solution 8.20N. in NaOH and 6.92N. in NaI. W. R. A.

Acetone-, ethyl alcohol-, dioxan-, and glycerol-water-lead chloride systems.—See A., 1944, I, 164.

Decrease of free surface energy as a basis for the development of equations for adsorption isotherms, and the existence of two condensed phases in films on solids. W. D. Harkins and G. Jura (*J. Chem. Physics*, 1944, 12, 112—113).—The adsorption of vapours on solid surfaces is part of the general behaviour of insol. adsorbed films on liquids and solids. The free energy of the surface is the fundamental basis for the treatment of this subject. Equations giving the pressure-area relations of insol. oil films on H_2O should and do apply to adsorbed films on solids or on other liquids. Two such equations (linear) are formulated. When applied to films on solids the plot exhibits two straight lines, thereby indicating the existence in the film of two condensed phases with a second-order transition. Examples of this are films of PrOH on BaSO_4 or anatase and films of N_2 on certain catalysts used in the petroleum industry and on certain charcoals. C. R. H.

Condensation and supersaturation of adsorbed phases. H. M. Cassel (*J. Chem. Physics*, 1944, 12, 115—116).—The validity of Langmuir's adsorption isotherm is discussed in view of the interaction of neighbouring adatoms not having been taken into account. Starting with the Emmett-Brunauer-Teller adsorption isotherm and eliminating surface density, it can be shown that the surface tension of adsorbed, built-up film (presumably liquid) is negative. This conclusion is due to disregarding lateral cohesion in the design of the film model. If mutual attraction of adatoms is taken into account, cluster formations and phase transitions leading to metastable mono- or multi-layers are to be expected. Existence of the latter is possibly indicated in the observed hysteresis in capillary condensation. C. R. H.

Van der Waals adsorption of H_2 , D_2 , CH_4 , N_2 , and Ne on nickel plates. A. van Itterbeek and J. Borghs (*Z. physikal. Chem.*, 1941, B, 60, 128—142).—The van der Waals adsorption has been measured for H_2 , D_2 , CH_4 , and N_2 at the temp. of liquid N_2 , and for Ne, H_2 , and D_2 at the temp. of liquid H_2 , on Ni platelets of known macroscopic surface area. The results for N_2 , Ne, and CH_4 agree with the Polanyi potential theory, and satisfy the equations $q_A(v)/q_B(v) = (a_A/a_B)^{1/2}$, $Q - q + q_i [q_A(v)] =$ the adsorption potential function of gas A, at adsorption vol. v , a — van der Waals const., Q — experimental ΔH of adsorption, q — the Polanyi potential energy, and $q_i = \Delta H$ of vaporisation. H_2 and D_2 at the temp. of liquid H_2 possess a potential function which differs from the Polanyi function, is dependent on T , and is such that the potential of $\text{H}_2 > \text{D}_2$. $q_{\text{D}_2}(0)/q_{\text{H}_2}(0) \sim 1$, as for H_2O and D_2O on glass plates at room temp., and for H_2 and D_2 on charcoal at liquid H_2 temp. The microscopic surface area of the Ni plates, calc. from the vals. of the const. v_m of the multilayer theory of Brunauer, Emmett, and Teller (A., 1938, I, 190), was ~ 5 times the macroscopic surface area. W. R. A.

Adsorption of gases on smooth surfaces of steel. M. H. Armbruster and J. B. Austin (*J. Amer. Chem. Soc.*, 1944, 66, 169—171).—The adsorption of A, Ne, H_2 , N_2 , CO, and CO_2 on three samples of cold-rolled steel has been determined at 20°, —78°, —183°, and —195° and at pressures up to 0.12 cm. The measurements were made first on the grease-free, outgassed surface, and then on the same surface after reduction in H_2 . Numerous preliminary adsorptions and desorptions were necessary before the results were reproducible. H_2 and Ne are not measurably adsorbed on either surface under these conditions. A monolayer of physically adsorbed N_2 , A, or CO is formed on the unreduced surface at —183°, but $\sim 15\%$ of each gas cannot be desorbed by reducing the pressure. On the reduced surface, N_2 and A form physically adsorbed monolayers, which can be completely removed by reducing the pressure; sorption of a similar monolayer of CO is partly chemisorption. CO_2 is measurably adsorbed on both surfaces at —78°. The isotherms, although similar to the saturation type, probably represent the low-pressure sections of sigmoid isotherms. ΔH of adsorption, calc. by the equation of Brunauer *et al.* (A., 1938, I, 190), is ~ 3 kg.-cal. per mol. for all physical adsorption, and depends more on the nature of the surface than on the chemical nature of the adsorbate. $v = v_s \{ap / (1 + ap)\}^{1/n}$ (v = vol. adsorbed at pressure p , v_s = vol. adsorbed at saturation, a , n are consts.), a combination of the Freundlich (low-pressure) and Langmuir (higher-pressure) equations, represents the isotherms over the complete range of pressures. n , which decreases with T , is a measure of the deviation of the adsorbed film from an ideal two-dimensional gas. When some of the gas is strongly adsorbed, the force/area curves exhibit phase transformations similar to those of monolayers on H_2O . The sp. surface of the samples was 4 times the geometrical surface. W. R. A.

Effect of neutral salts on the adsorption of alkalis by silica. Y. Fu (*J. Chinese Chem. Soc.*, 1943, 10, 103—112).—Neutral salts cause increase in the adsorption of NaOH and KOH by SiO_2 as measured by titration with acid, but the adsorption of the cation is

decreased. The adsorption from the mixtures follows the Freundlich law. An explanation based on hydrolytic adsorption of the neutral salts is proposed and applied to other cases. J. H. BA.

Antonoff's so-called rule. H. L. Cupples (*J. Physical Chem.*, 1944, 48, 75—76).—It is impossible to predict from the considerations advanced by Yoffe and Heymann (cf. A., 1943, I, 276) whether the work of adhesion for org. liquid- H_2O is $>$ or $<$ the work of cohesion of org. liquid saturated with H_2O , or whether, therefore, the equilibrium spreading coeff. is zero (as required by Antonoff), negative, or positive. C. R. H.

Equations for the pressure-area relations (isotherms) of liquid-expanded and intermediate monolayers on water. G. Jura and W. D. Harkins (*J. Chem. Physics*, 1944, 12, 113—114).—The linear equations referred to earlier (cf. A., 1944, I, 151) are not applicable to liquid-expanded or to liquid intermediate phases on an aq. subphase. Empirical logarithmic equations are proposed for such cases. C. R. H.

Existence of expanded and intermediate phases in films on solids. G. Jura and W. D. Harkins (*J. Chem. Physics*, 1944, 12, 114).—The logarithmic equations developed for insol. monolayers on H_2O in the liquid-expanded and intermediate phases (cf. preceding abstract) are valid for adsorbed C_4H_{10} on porous catalysts at 0°. C. R. H.

Permeability of built-up fatty acid films towards molecules and ions. D. Beischer and G. Oeschel (*Z. Elektrochem.*, 1943, 49, 310—315).—Stearic acid-Ba stearate and arachidic acid-Ca arachidate multilayers on Cu, built up by the method of Blodgett (A., 1935, 931), hinder but do not stop completely the tarnish of the metal in H_2S . Similar films on Ag cause a more rapid and more intense attack on the metal in I vapour, max. attack being observed when the layer is 3 mols. thick. This is attributed to the high solubility of I in the film. Coating of Cd with a single film greatly reduces attack in aq. CuSO_4 whilst a film 5 layers thick prevents attack completely, showing it to be impermeable to Cu^{++} ions. On using a Cu sheet partly covered by a single film as cathode in aq. CuSO_4 , no Cu deposits on the area covered by the film, whilst if the whole surface is covered by a film deposition occurs only where the film breaks down on the irregularities of the surface. "Skeleton" films produced by dissolving the arachidic acid from the films are much more permeable. The built-up films are not very strong mechanically and are easily damaged by rubbing. J. W. S.

Modified diffusion in membranes. R. E. Liesegang (*Ann. Physik*, 1941, [v], 39, 326—329).—The rate of diffusion of methylene-blue solution through a paper membrane floating on its surface is modified by air currents incident on its surface, by access of moisture through its cut edges, and by damage to the membrane surface. L. J. J.

Atomic arrangement in aluminium hydroxide gel. S. Geiling and R. Glocker (*Z. Elektrochem.*, 1943, 49, 269—273).—Using monochromatic Cu X-radiation interference rings have been obtained with α - and β -hydrated Al_2O_3 gels, but Fourier analysis indicates that the α -gel has no space-lattice structure. J. W. S.

Silicic acid gels. XV. Effect of temperature on the time of setting of alkaline gel mixtures. C. B. Hurd, R. C. Pomatti, J. H. Spittle, and F. J. Alois. XVI. Effect of radiant energy on time of set. C. B. Hurd and W. U. Day (*J. Amer. Chem. Soc.*, 1944, 66, 388—390, 391—392).—XV. The time of setting of silicic acid gels, prepared from Na silicate and AcOH , has been determined at 0°, 25.1°, and 38.5° and at pH 6.8—10.73. At pH > 10.5 rise in temp. increases time of set, but at pH < 10 the effect is reversed. Owing to curvature in the plot of \log (time of set) against T , ΔE of activation could not be calc. The temp./time of set relation at pH > 10 is ascribed to a temp.-acceleration of dissolution of the gel being $>$ acceleration of its formation. At pH > 11 , acceleration of dissolution is predominant, and gels do not form. pH increases during setting of gels at pH > 10 , possibly because of a decrease in ionisation with increase in the complexity of the polysilicic acid. No thermally reversible gels were found. Alkaline gels are softer and less elastic than acid gels, as condensation and cross-linking are probably not so extensive.

XVI. The effect of radiation on the time of set of Na silicate- AcOH gels has been investigated. Illumination by an incandescent lamp, a capillary Hg arc, and an Fe spark produced no observable effects. Determination of the absorption of radiation at 4000—7000 Å. by the sol before setting indicates an absorption increasing with age, the greater increase taking place at the lower λ . W. R. A.

Thermodynamics of heterogeneous polymer solutions. P. J. Flory (*J. Chem. Physics*, 1944, 12, 114—115).—Thermodynamic equations for polymer solutions, where the polymers are composed of numerous species differing in mol. size, have been deduced. Their applicability to solubility and fractional pptn. and dissolution is forecast. C. R. H.

Study of the flexibility of macro-molecules with ultrasonic waves. G. Schmid and E. Beuttenmüller (*Z. Elektrochem.*, 1943, 49, 325—334).—Solutions of polystyrene (I) (mean mol. wt. 150,000—200,000) in various binary mixtures of PhMe, CCl_4 , COMe_2 , cyclohexane, and MeOH of differing d have been treated with ultrasonic waves for

various times and the mol. wt. of the solute has been determined viscometrically. The relative η of solvent and solute has no essential effect on the depolymerisation, and especially when they have equal η the solvent does not decrease the degree of depolymerisation. It is inferred that the depolymerisation is due to a difference in the ease of deformation of (I) and solvent mols., the gel framework being very rigid at least during the period of one ultrasonic wave and being capable of an independent conduction of the vibration over a considerable distance. J. W. S.

Sedimentation and diffusion measurements on cellulose and cellulose derivatives. N. Gralén (*Thesis, Uppsala*, 1944, 115 pp.).—The principles of sedimentation using the ultracentrifuge are described, and an empirical relation between rate of sedimentation and concn. is given. Taking this into account the shape of the sedimentation curve for polydisperse systems is analysed mathematically. The width of the curve is regarded as a measure of the polydispersity. Sedimentation experiments are performed on cellulose (I) in cuprammonium solution, cellulose nitrate (II) in COMe, Na cellulose xanthate (III) in aq. alkali, and Na cellulose glycolate (IV) in H₂O. Apparatus and precautions for preparing and transferring cuprammonium solutions in a N₂ atm. are described. Data are given for native fibre celluloses (unbleached and bleached) and for several wood celluloses. The effects of different chemical treatments in reducing the sedimentation consts. are evident; in general a reduction in sedimentation const. is accompanied by an increase in polydispersity. (II) of N content ~13.8% are prepared by nitration of several (I) in HNO₃-H₂PO₄-P₂O₅ mixtures. The sedimentation curves are similar in shape to those of (I). Only a few measurements on (III) and (IV) are recorded. Apparatus for diffusion measurements, based on change of n , is described, and measurements are made on the same materials as above. The skewness of diffusion curves arises from the dependence of the diffusion const. on concn. Diffusion of a polydisperse substance is treated mathematically, and a method for determining the polydispersity suggested. For (I) the diffusion process reaches its true velocity only after the lapse of some time. The derivatives of (I) behave normally. A formula is derived for determining mol. wts. from sedimentation equilibrium (equilibrium between sedimentation and diffusion). Equilibrium is reached in a reasonable time only for (I) of fairly low mol. wt. The partial sp. vol. of (I) was found to be 0.664. Mol. wts. of (I) and its derivatives determined by sedimentation and diffusion are reviewed, and shown to differ from those obtained from η measurements, using Staudinger's relation. The relation between intrinsic η and mol. wt. is not linear. Comparison of mol. wts. of (I) and (II) shows that some depolymerisation takes place in nitration (~3 bonds per 10,000 ruptured). (III) and (IV) have relatively low mol. wts. Approx. data for the shape of mols. are given; (I) mols. are less fully extended than (II) mols. The polydispersity of each substance tends to increase with decreasing mol. wt., but (II) has rather lower polydispersity than corresponding (I), indicating that the larger mols. are preferentially degraded during nitration. Results from sedimentation and diffusion are not usually in good agreement, but the experimental errors and approximations involved are considerable. Full references are given. R. H. F.

Interpretation of the cellulose-water adsorption isotherm and data concerning the effect of swelling and drying on the colloidal surface of cellulose. A. G. Assaf, R. H. Haas, and C. B. Purves (*J. Amer. Chem. Soc.*, 1944, 66, 66—73).—Three highly swollen celluloses were subjected to TIOEt and then MeI and finally analysed for OMe. The results, extrapolated to solvents having mol. vol. 18 and 35, give % theoretically accessible to H₂O vapour and N₂, respectively. H₂O-adsorption at 20° and 25° is determined; the final change in direction of the isotherm (at R.H. ~50%) occurs at ~1 H₂O per accessible OH in the cellulose, which is interpreted as being equiv. to a unimol. layer of H₂O over the accessible surface; the first change in direction of the isotherm (at R.H. ~10%) corresponds to adsorption of 1 H₂O per primary OH. The flatter portion of the isotherm corresponds to adsorption by sec. OH and cannot occur at >80%. 98% of the surface of moist, swollen cellulose is destroyed by drying, but >25% is lost by solvent-exchange. Adsorption of 6—9% of H₂O increases the colloidal surface of highly swollen cellulose by ~20% but that of unswollen samples 30-fold. R. S. C.

VI.—KINETIC THEORY. THERMODYNAMICS.

Determination of order of reaction. Dissociation constant of hypochlorous acid. J. M. González Barredo (*Anal. Fís. Quím.*, 1940, 36, 328—331).—Experimental errors are greatly magnified in the calculation of dissociation consts. as shown by the wide variation of the vals. for the decomp. of HOCl. The order of this reaction cannot be determined by the author's method (cf. A., 1936, 1074).

F. R. G.

Potentiometric measurements of hydrogen-ion concentration in solutions of low dielectric constant. A. Gemant (*J. Chem. Physics*, 1944, 12, 79—88).—E.m.f. (glass electrode) and conductivity

measurements have been made on dioxan solutions of *p*-C₆H₄Me-SO₃H (I), CCl₃-CO₂H, and HCl and on xylene solutions of (I) and picric acid. The acids behave essentially as weak electrolytes, deviations from the mass law being explainable on the basis of varying dielectric const. with varying acid concn. H transference nos. and the ionic radii of the acids in the solvents have been calc. from the data. The use of a cell consisting of two half-cells in which the solutions have slightly different dielectric const. is described. C. R. H.

Solution theory and pH measurements. P. G. Nutting (*J. Franklin Inst.*, 1943, 236, 573—580).—A general theory of electrolytic solutions is outlined. Exact buffer equations indicate that when very dil. alkali is titrated with very dil. acid the pH at first increases and then decreases; the converse happens in titrating very dil. acid with alkali. It is shown that a linear relation between pH and log concn. is consistent with exact solution theory. An extension of the theory to conditions where ion adsorption may take place is discussed with special reference to the operation of the glass electrode where the presence of different anions, each with its own adsorption coeff., none of which is able to overpower the others, may result in multiple pH readings or buffer points. C. R. H.

Thermodynamic study of lead chloride in dioxan-water by means of electromotive force and solubility data at 25°. The acetone ethyl alcohol-, dioxan-, glycerol-water-lead chloride systems. M. V. Noble and A. B. Garrett (*J. Amer. Chem. Soc.*, 1944, 66, 231—235).—The e.m.f. of the cell Pb(Hg)[PbCl₂][AgCl]Cl has been measured at 25° in 20, 40, and 60% dioxan-H₂O mixtures, [PbCl₂] varying from 4.24 × 10⁻⁴M. to saturation. The solubility of PbCl₂ has been determined in dioxan-H₂O mixtures containing various concns. of added KCl or KNO₃, and in EtOH-H₂O, glycerol-H₂O, and COMe-H₂O mixtures. Activity coeffs. and solubility products have been computed for dioxan-H₂O. Divergences in the slopes of the plot of -log γ against $\mu^{\frac{1}{2}}$ are attributed to association. W. R. A.

Thermal analysis of binary systems. (A) A. Stock. (B) L. Kofler and A. Kofler (*Ber.*, 1941, 74, [B], 1049, 1050).—(A) Priority is claimed for Stock (A., 1909, ii, 543) (cf. Rheinboldt, A., 1943, I, 308). (B) The original priority is much antecedent. R. S. C.

Phase equilibria in hydrocarbon systems. Methane-carbon dioxide in the gaseous region. H. H. Reamer, R. H. Olds, B. H. Sage, and W. N. Lacey (*Ind. Eng. Chem.*, 1944, 36, 88—90).—Pressure-vol. relations over the ranges 38—238° and 100—10,000 lb. per sq. in. for CO₂ and for four CO₂-CH₄ mixtures have been determined. Compressibility factors are tabulated. The simple behaviour of CH₄-rich mixtures at all pressures investigated suggests that the effect of small concns. of CO₂ on the behaviour of gaseous hydrocarbons can be satisfactorily predicted. C. R. H.

Solid-liquid phase equilibria of the system *p*-toluidine-acetic acid. W. W. Lucase, R. P. Koob, and J. G. Miller (*J. Physical Chem.*, 1944, 48, 85—89).—Determination of the m.p. curve of the system confirms the existence of *p*-C₆H₄Me-NH₂·2AcOH (m.p. 49.1°). The m.p. of the eutectics at 30.2 and 89.7 mol.-% of AcOH are 28.6° and 6.4° respectively. C. R. H.

Normal mixed crystal formation with some so-called group-isomorphous substances. (Frl.) A. Kofler (*Z. physikal. Chem.*, 1942, A, 191, 241—247).—A short discussion. Contrary to previous reports, the systems C₁₀H₈- β -C₁₀H₇·OH (I) and - β -C₁₀H₇·NH₂ (II) exhibit normal isomorphism and isodimorphism respectively. An equimol. compound is formed in the system (I)-(II), which is completely miscible with (I) and partly miscible with (II). The appearance of a mol. compound does not exclude the possibility of mixed crystal formation; indeed this may be favoured when the crystal units of the components are double mols. J. F. H.

System ammonium nitrate-sodium nitrate. E. O. Holmes, jun., and D. Reinson (*J. Amer. Chem. Soc.*, 1944, 66, 453—457).—The system NH₄NO₃-NaNO₃ has been re-examined over the range 0—35 wt.-% NaNO₃. Solubility curves for the two forms of NH₄NO₃ are linear whilst that for NaNO₃ is parabolic. The eutectic temp. is 121.2 ± 0.2° and the transition temp. 126.2 ± 0.2°; the eutectic composition is 21.0 ± 0.1 and the transition composition is 18.0 ± 0.1 wt.-% NaNO₃. The method of purification of NaNO₃, the length of time of drying, and the size of the sample appear to have no effect on the temp. of disappearance of the last crystal on heating the melt. W. R. A.

Phase relations in the system calcium orthosilicate-orthophosphate. M. A. Bredig (*Amer. Min.*, 1943, 28, 594—601).—A discussion. Two different crystal structures, isotypic with hexagonal α - and orthorhombic β -K₂SO₄, occur in Ca₂SiO₄ containing small amounts of various additions. This, and the fact that γ -Ca₂SiO₄ is isotypic with β -Na₂BeF₄, the high-temp. α form of which is also isotypic with α -K₂SO₄, indicates that above 1420° Ca₂SiO₄ is isodimorphous with K₂SO₄. A schematic equilibrium diagram of the system Ca₂SiO₄-Ca₃(PO₄)₂ is given. L. S. T.

Ternary system dioxan-benzene-water. R. J. Berndt and C. C. Lynch (*J. Amer. Chem. Soc.*, 1944, 66, 282—284).—The isotherm of the dioxan-C₆H₆-H₂O system at 25° has been determined. An analysis diagram for the miscible region of the system and vals. of

n_2^5 and p_4 for dioxan- C_6H_6 mixtures and for the ternary system are given. Phase equilibria in the ternary system satisfy the relation employed by Bancroft *et al.* (A., 1942, I, 240) for several ternary liquid systems. W. R. A.

System potassium carbonate-sodium carbonate-water at 100° and 150°. G. Ervin, jun., A. L. Giorgi, and C. E. McCarthy (*J. Amer. Chem. Soc.*, 1944, 66, 384—387).—The system K_2CO_3 - Na_2CO_3 - H_2O at 100°, studied by the usual chemical methods and by microscopic and X-ray examination, gives an isotherm with branches corresponding with $K_2CO_3 \cdot 1.5H_2O$, $K_2CO_3 \cdot Na_2CO_3$, and $Na_2CO_3 \cdot H_2O$, whilst the three branches of the 150° isotherm correspond with $K_2CO_3 \cdot 1.5H_2O$, $K_2CO_3 \cdot Na_2CO_3$, and Na_2CO_3 . The double salt, which exists to a slightly greater extent at 150°, is incongruently sol. at 100° and 150° and, in contact with H_2O , decomposes to give solid $Na_2CO_3 \cdot H_2O$ or Na_2CO_3 and a solution relatively richer in K_2CO_3 . W. R. A.

The lines in quaternary liquid systems. J. C. Smith (*Ind. Eng. Chem.*, 1944, 36, 68—71).—A graphical method of representing equilibria in quaternary liquid systems, which is based on data for the system $CHCl_3$ - $COMe$ - $AcOH$ - H_2O , is described. The application of the method to the solution of problems in mixed solvent extraction is described. C. R. H.

Graphical representation of the thermodynamic potential in multi-component systems. G. Masing (*Z. Elektrochem.*, 1943, 49, 216—218).—Although for a binary mixture $d\zeta/dc = +\infty$ and $d^2\zeta/dc^2 = +\infty$ for $c = 0$ or 100% (c = concn. of one component), the radius of curvature of the ζ - c curve is zero at $c = 0$ or 100% and hence this curve does not meet the pure component axes tangentially. It is derived graphically that for a binary system in which a compound of congruent m.p. is formed, the liquidus curve at the temp. max. is continuous and has a horizontal tangent, whilst at the eutectic point the primary crystallisation curve forms a finite angle to the concn. axis. J. W. S.

Principles of thermodynamics. B. Leaf (*J. Chem. Physics*, 1944, 12, 89—98).—A formulation of thermodynamics which has been developed demonstrates the limitations of the classical treatment and leads to an equation for entropy (S) produced and heat dissipated in irreversible processes. A generalised form of the second law of thermodynamics has been deduced. The new concepts have been applied to discussions on the phase rule, the derived functions H ($=E + PV$), A ($=E - TS$), F ($=H - TS$) where E = energy and P , V , and T have their usual significance, and to generalisations of Kelvin's postulate and the Carnot cycle. The principles of Bronsted's system of energetics have also been derived. C. R. H.

Thermochemistry of chlorine monoxide. W. A. Roth (*Z. physikal. Chem.*, 1942, A, 191, 248—250).—The results of Secoy and Cady (A., 1942, I, 19) on the partial pressures (p) of Cl_2O over aq. solutions of Cl_2O and $HOCl$ are combined with the author's earlier determination of the hydrolysis const. of Cl_2O aq. (A., 1930, 163), to obtain Henry's coeff. (K) for the system. With p expressed in mm., $K = 0.0093 \pm 0.00005$ at 3.46°. The true solubility of Cl_2O is five times that of Cl_2 . J. F. H.

Heats of dilution of sodium chloride in ethylene glycol at 25°. W. E. Wallace, L. S. Mason, and A. L. Robinson (*J. Amer. Chem. Soc.*, 1944, 66, 362—365).—Heats of dilution of $NaCl$ in $(CH_2OH)_2$ have been measured from 0.0001 to 0.17M. at 25°, and equations for the relative apparent molal heat content of the solute and for the relative partial molal heat contents of the solute and solvent have been derived. The experimental data agree with the calc. vals. W. R. A.

Calculation of heat of mixing from the phase diagram. E. Scheil (*Z. Elektrochem.*, 1943, 49, 242—254).—The method of calculating the heat of mixing from the phase diagram of a binary mixture is described. The theory developed is applied to the systems Zn-Pb, Zn-Bi, Ni-Au, Zn-Cd, and Cu-Ag. The heat of mixing of mixed phases is also discussed. J. W. S.

Entropy of argon. K. Clusius and A. Frank (*Z. Elektrochem.*, 1943, 49, 308—309).—The b.p. of A has been redetermined as $87.29 \pm 0.02^\circ K$. From calorimetric data the entropy of A at the b.p. is 30.850 ± 0.10 entropy units, compared with the statistical val. of 30.860 entropy units. From these vals. the v.p. and entropy consts. are 0.808 ± 0.020 and 0.810 , respectively. J. W. S.

Thermochemistry of alloys. X. Entropy change during alloy formation. O. Kubaschewski and A. Schneider (*Z. Elektrochem.*, 1943, 49, 261—269).—The entropy of formation of alloys is discussed theoretically. Entropy-composition curves for several alloys, deduced from thermochemical and e.m.f. measurements, are given. J. W. S.

VII.—ELECTROCHEMISTRY.

Temperature coefficients of electrical conductance of solutions containing sodium chloride, potassium chloride, magnesium sulphate, or their mixtures. R. W. Bremner (*J. Amer. Chem. Soc.*, 1944, 66,

444—446).—The coeffs. of the equation $\Lambda = a + b\theta + c\theta^2 + d\theta^3$ have been calc. from previous data on aq. KCl , $NaCl$, $MgSO_4$, $NaCl-KCl$, and $NaCl-MgSO_4$ (Bremner *et al.*, A., 1939, I, 15, 373), the average deviation from experimental vals. being 0.006%. Temp. coeffs., $d\Lambda/dt$, at 5° intervals between 0 and 25°, have been calc. from this equation. Temp. coeffs. of sp. conductance have been calc. for the conductivity H_2O used, and for 0.01 and 0.1 demal standard KCl solutions, at 5° intervals from 0 to 25°, and at 18°. The relations between temp. coeffs. and changes in concn. or temp., or the addition of a second salt, are discussed. W. R. A.

Mobility of the hydrogen ion in water-dioxan mixtures. H. Hartmann (*Z. physikal. Chem.*, 1942, A, 191, 197—212).—An equation is deduced for the mobility of H^+ ions in mixed solvents on the assumption of an exchange mechanism between H_3O^+ and H_2O , using the postulates of the Hückel theory. Vals. of d , η , and ϵ for H_2O -dioxan mixtures were determined over the entire solubility range and at 20—70°. The conductivity of various dil. solutions of HCl in H_2O -dioxan mixtures (0—60 mol.-% dioxan) was determined at 20—60°, and hence the corresponding equiv. conductivity at infinite dilution. The results are in qual. agreement with the deduced equation. J. F. H.

Mechanism of migration of the hydrogen ion in aqueous solution and its behaviour in diffusion processes. H. Hartmann (*Z. physikal. Chem.*, 1942, A, 191, 213—226).—Theoretical. From the postulates of the Hückel theory of the anomalous mobility of the H^+ ion in aq. solution, the Nernst equation for the mobility of the H^+ ion is derived. Comparison of this equation with diffusion data gives discrepancies experimental error. The migration mechanism suggested by Wulff and Hartmann (A., 1944, I, 87) expresses the results better than that of Hückel. J. F. H.

Concentration distribution in two-salt moving boundaries. L. G. Longworth (*J. Amer. Chem. Soc.*, 1944, 66, 449—453).—The movement of KIO_3 - KCl and $LiCl$ - KCl concn. boundaries under an applied potential has been studied by the schlieren scanning method. With const. current the concn. distribution is independent of time, and is accurately given by Weber's theory. The adjusted concn., and, hence, the transference no., of the indicator electrolyte (KIO_3 , $LiCl$) may be determined from the schlieren photographs. W. R. A.

Cu-Cu⁺ potential in concentrated copper sulphate solutions at various temperatures. III. Temperature coefficient of the normal potential of copper. F. Müller and H. Reuther (*Z. Elektrochem.*, 1943, 49, 277—280).—From e.m.f. measurements on cells of the type $Cu|CuSO_4, H_2SO_4, Hg_2SO_4|Hg$ the temp. coeff. of the normal electrode potential at 20—50° has been determined as 0.01 mv. per degree. This low val. is accounted for by the temp. coeff. of the potential of this electrode being almost equal to that of the H_2 electrode. The calculation of an isothermal temp. coeff. from two non-isothermal vals. for half-cells is discussed. J. W. S.

Polarographic behaviour of aniline oxidation products. D. Lester and L. A. Greenberg (*J. Amer. Chem. Soc.*, 1944, 66, 496).—The oxidation of $NHPh \cdot OH$ (I), $p-NH_2 \cdot C_6H_4 \cdot OH$, and azoxybenzene (II) at the dropping Hg cathode has been studied. In 0.07M-phosphate buffer (pH 6.3), (I) does not give a cathodic wave, but does give an anodic oxidation wave with a half-wave potential, against the saturated Hg_2Cl_2 electrode, of -0.02 v. in contrast to the results of Levitan *et al.* (A., 1944, I, 130), who find a cathodic wave in 0.1M- $NaOH$, but no anodic wave. In the presence of alkali, (I) is converted completely into (II), which gives a cathodic wave. Two electrons are involved in the oxidation of the buffered solution of (I), whereas the reduction of (II) in the same buffer containing 20% of $EtOH$ involves four electrons. W. R. A.

Electrolytic reduction of aqueous chromic acid solutions. E. Müller (*Z. Elektrochem.*, 1943, 49, 280—282).—The E - c curves (E = cathode potential, c = cathode c.d.) for the electrolysis of $2M-H_2CrO_4$ using Pt or Ir cathodes are almost identical with the curves obtained for these electrodes in $2M-H_2SO_4$, whereas the E - c curves for Cu and Au cathodes are displaced towards more negative vals. of E . After use the Cu and Au electrodes are covered with a dirty brown deposit of Cr, and hence the displacement of the E - c curve is attributed to the higher overpotential of H_2 at a Cr surface although the E - c curve for a massive Cr electrode lies towards even higher vals. of E . The mechanism of the deposition of the Cr is discussed. J. W. S.

Uses and limitations of membrane electrodes. C. E. Marshall (*J. Physical Chem.*, 1944, 48, 67—75).—The difficulties which arise in the measurement by means of membrane electrodes of ionic activities in true solutions are discussed. The probable uncertainty of measurement is $>4\%$ at ionic strengths $\sim 0.1M$, and $\sim 2\%$ at ionic strengths $< 0.01M$. The properties of montmorillonite and beidellite membranes and the effect of thermal pretreatment are reviewed, and a method of analysing mixtures by determining the mobility ratio of two cations within a given membrane is outlined. C. R. H.

VIII.—REACTIONS.

The rate-determining reaction in chain reactions, particularly polymerisation reactions. G. V. Schulz (*Z. physikal. Chem.*, 1941, B, 50, 116—123).—The concept of the rate-determining reaction in chain reactions is discussed with reference to the polymerisation of styrene (I) and $\text{CH}_2=\text{CMe}-\text{CO}_2\text{Me}$ (II). It is shown that, in polymerisation reactions, where no stoichiometric relation exists between the various steps, there can be no rate-determining reaction. The concept can be replaced by a consideration of which process in the chain is directly influenced by a particular change in conditions. Special cases exist, in which a rate-determining reaction can be defined, e.g., the Bz_2O_2 -catalysed polymerisation of (I) or the atm. O_2 -catalysed polymerisation of (II), where the primary process consists of two or more steps, stoichiometrically related.

W. R. A.

Mathematics of polymerisation.—See B., 1944, II, 125.

Reaction of acetaldehyde with ethyl bromide at 400°. J. G. Roof (*J. Amer. Chem. Soc.*, 1944, 66, 358—360).—The dark reaction of mixtures of MeCHO and EtBr at 400°, studied by pressure measurements and analysis of the products, shows a pronounced induction period of an autocatalytic type in the early stages of the reaction. A sharp decrease in the rate of pressure rise occurs after an increase of ~ 1.1 times the original partial pressure of MeCHO . On the average ~ 10 mols. of MeCHO are decomposed per mol. of EtBr .

W. R. A.

Allylic rearrangements. XIV. Hydrolysis of butenyl chlorides. W. G. Young and W. J. Andrews (*J. Amer. Chem. Soc.*, 1944, 66, 421—425).—The hydrolyses of crotyl (I) and methylvinylcarbinyl (II) chlorides have been studied under conditions designed to produce different S_N1 to S_N2 ratios, and the composition of the resulting butenols has been determined. (II) reacts by the S_N1 process to give a mixture of allylic isomerides, whereas (I), which is very sensitive to changes in conditions, reacts by both processes, giving more of the normal reaction products when a bimol. reaction is favoured. Kinetic studies of the hydrolysis of (I) and (II) by NaOH in $\text{EtOH}-\text{H}_2\text{O}$ show that the reaction rate with (II) is independent of $[\text{OH}^-]$, whereas (I) undergoes both first- and second-order reactions. The first-order reaction of (I) is partly a bimol. reaction with the solvent.

W. R. A.

Semi-polar bond. Its effect on chemical reactivity. Hydrolysis of phosphorus trichloride and oxychloride. J. Rodriguez de Velasco and R. Castro Ramos (*Anal. Fis. Quím.*, 1942, 38, 171—178).— k for the hydrolysis of PCl_3 and POCl_3 in PhMe is respectively 9.3×10^{-2} and 1.8×10^{-2} at 20°, and 13.0×10^{-2} and 3.7×10^{-2} at 35°. It is concluded that the semi-polar bond in POCl_3 causes a reduction in k .

F. R. G.

Kinetics of transformation of 2-ketopolyhydroxy-acids. P. P. Regna and B. P. Caldwell (*J. Amer. Chem. Soc.*, 1944, 66, 246—250).—The kinetics of the consecutive reactions of 2-keto- d -gluconic, l -gulonic, d -galactonic, d -glucoheptonic, d -galactoheptonic, and of l -, d -, d -arabo- d -gluco-, and d -galacto-ascorbic acid in 5M-HCl at 59.9° and 69.9° have been investigated. Rates of rearrangement of the 2-ketopolyhydroxy-acids to their ascorbic acid analogues are influenced by groups on the C atoms outside the lactone ring. Rate coeffs. of the decomp. of ascorbic acids are higher for a *cis*- than for a *trans*-arrangement of the H atoms on $\text{C}_{(4)}$ and $\text{C}_{(5)}$. A method is described for determining the rate coeffs. of the reaction system $A \rightarrow B \rightarrow C$, where only B can be determined experimentally.

W. R. A.

Hydrolysis of pantothenate; a first-order reaction. Relation to thiamin stability. D. V. Frost and F. C. McIntire (*J. Amer. Chem. Soc.*, 1944, 66, 425—427).—The hydrolysis of Ca pantothenate (I) has been studied in aq. solution of pH 3.7—4.0 at temp. of 10—100°. The hydrolysis is a first-order reaction, with a rate independent of the type of buffer used. ΔE of activation is 19 ± 1 kg.-cal. per mol. The effect of pH on the rate of decomp. of (I) and of thiamin hydrochloride (II) has been determined at pH 3—7. Decomp. of (I) is reduced and decomp. of (II) increased by increasing pH.

W. R. A.

Kinetics of the antioxygenic synergism of quinones with ascorbic acid in fat systems. V. P. Calkins and H. A. Mattill (*J. Amer. Chem. Soc.*, 1944, 66, 239—242).—The abs. reaction rate of oxidation of ascorbic acid (I) in the Et esters of lard fatty acids has been determined in presence and absence of benzoquinone (II). The synergism of (II) with (I), in the stabilisation of the esters, is due to the catalytic action of (II), which is reduced to a semiquinone, capable of reducing the fat peroxides. (II) reduces the ΔG of formation of the activated complex in the fat-(I) system, so that the no. of (I) mols. possessing the necessary energy of reaction is doubled. A mechanism for the synergism, based on the views of Michaelis (*Chem. Rev.*, 1935, 16, 243), is developed.

W. R. A.

Decomposition of chloral hydrate by piperidine.—See A., 1944, II

Active materials. LXII. Catalytic behaviour of preparations of $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3 + \text{BeO}$ made in different ways. R. Fricke and G. Wessing (*Z. Elektrochem.*, 1943, 49, 274—277).—At 177.2° the

catalytic dehydrogenation of Pr^2OH on an activated Al_2O_3 surface is of zero order. The velocity of reaction v increases initially with time but finally becomes const. with any particular specimen of catalyst. The energy of activation (E) of the reaction increases with increasing temp. of preheating of the catalyst. Max. v was obtained with carefully purified pptd. Al_2O_3 preheated for 54 hr. at 600°. Less pure material similarly heated showed similar E but gave much lower v owing to a decrease in the action const. C of the Arrhenius equation $k = Ce^{-E/RT}$. Addition of 2—4% of BeO to the Al_2O_3 has practically no effect on E but decreases v . With mixtures containing 50 mol.-% of BeO and with pure BeO v is much decreased and the reaction is no longer of zero order.

J. W. S.

Hydrocarbon synthesis by Friedel and Crafts' reactions. H. Ulrich, A. Keutmann, and A. Georhaas (*Z. Elektrochem.*, 1943, 49, 292—296; cf. A., 1935, 1207).—Study of the kinetics of the reactions with and without the introduction of dry HCl indicates that the addition of C_2H_4 to C_6H_6 with AlCl_3 as catalyst occurs both through the intermediate formation of EtCl and also directly as a surface reaction on the AlCl_3 , whereas with GaCl_3 as catalyst it is exclusively a surface reaction on the catalyst. InCl_3 does not catalyse the reaction. GaCl_3 is a more efficient catalyst than AlCl_3 , the max. efficiency being attained at 55°; the main product is PhEt , with smaller amounts of homologues than are obtained with AlCl_3 .

J. W. S.

Catalytic effect of acetate and phosphate buffers on the iodination of tyrosine. C. H. Li (*J. Amer. Chem. Soc.*, 1944, 66, 228—230).—The catalytic effect of PO_4^{3-} and OAc^- buffers on the I-tyrosine reaction at 25° has been studied. In PO_4^{3-} buffer, the sp. rate, $k_2 = 10^3[\text{OH}^-] + 150[\text{HPO}_4^{2-}] + 12[\text{H}_2\text{PO}_4^-]$. In OAc^- buffer, $k_2 \propto [\text{OAc}^-]/[\text{H}^+]$. The complex anion $\text{OH} \cdot \text{CMeO}_2^-$ is suggested as the catalytic agent in OAc^- buffer.

W. R. A.

Kinetics of reactions between iodine and histidine. C. H. Li (*J. Amer. Chem. Soc.*, 1944, 66, 225—227).—From investigations of the kinetics of the I-histidine reaction, in citrate and PO_4^{3-} buffers at 25°, the formation of di-iodohistidine, similar to di-iodo-tyrosine formation, is indicated. In citrate buffer at 25°, the rate law is $-d[\text{histidine}]/dt = 2.5[\text{histidine}][\text{I}] + 1.2 \times 10^5[\text{histidine}][\text{HOI}]$. HPO_4^{2-} has a sp. catalytic effect on the rate.

W. R. A.

Electrolytic catalysis in the ammonolysis of 9-chloro-9-phenylfluorene by liquid ammonia. P. M. Williamson, R. C. Anderson, and G. W. Watt (*J. Amer. Chem. Soc.*, 1944, 66, 376—379).—The catalysis of the ammonolysis of 9-chloro-9-phenylfluorene by liquid NH_3 by NaCl , NaNO_3 , and NH_4NO_3 has been studied, and vals. for velocity coeffs. and ΔE of activation determined. The reaction is subject to electrolyte catalysis by NH_3 and non-onium salts. The relation to the theory of acid catalysis is discussed.

W. R. A.

Esterification under the catalytic influence of acid chlorides.—See A., 1944, II, 179.

Photolysis of hydroxylamine. R. N. Smith and P. A. Leighton (*J. Amer. Chem. Soc.*, 1944, 66, 172—177).—The photolysis of NH_2OH vapour at 1—4 mm. Hg pressure by ultra-violet radiation from a Zn arc has been studied. The ultra-violet absorption spectrum is continuous at $\lambda\lambda$ of 2350 to ~ 2000 Å. Absorption in this region causes photolysis to H_2 , N_2 , and H_2O , together with small amounts of N_2H_4 , N_2O , and NH_3 . Thermal decomp. at room temp. produces chiefly N_2 , NO , N_2O , H_2O , and NH_3 . At const. light absorption, the rate of formation of H_2 decreases with increasing NH_2OH pressure, and \propto (incident intensity) $^{3/2}$. The data support a photolysis mechanism involving NH_2 and OH radicals.

W. R. A.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Reaction of potassium chromate with an indium salt. M. F. Stubbs (*J. Amer. Chem. Soc.*, 1944, 66, 498).—Addition, with stirring, of 0.2222M- K_2CrO_4 to 0.02M- $\text{In}_2(\text{SO}_4)_3$ at room temp. was followed by pH measurement. A yellow turbidity appeared at pH 3.3, complete flocculation of the yellow ppt. occurred at 3.36—3.42, and pH rose steadily with further addition of K_2CrO_4 . Analysis data for the yellow ppt. suggest that it is formed either as $\text{In}_2(\text{CrO}_4)_3$ which is extensively hydrolysed or as a mixture of $\text{In}_2(\text{CrO}_4)_3$ and $\text{In}(\text{OH})_3$.

W. R. A.

Cuprous isothiocyanate. D. Kruger and E. Tschirch (*Ber.*, 1941, 74, [B], 1378—1386; cf. A., 1936, 1078).—The appearance of violet CuSCN with its characteristic c -lines in the X-ray spectrum is barely affected by the temp. at which it is prepared (0—70°). Heating this form at 150° changes the colour to pale yellow and at $\sim 275^\circ$ to grey but does not remove the c -lines or cause loss of wt. Differentiation of the forms crystallographically is shown to be erroneous. The occasional brown colour of the δ -form, particularly the parts crystallising later, is due to adsorbed I. Formation of the violet form is favoured by presence in solution of large amounts of certain neutral salts which, however, are not absorbed into the ppt. Differences between the forms are due to arrangement of Cu⁺, S, C, and N in the crystal lattice.

R. S. C.

Formation, reducibility, and extractability of zinc ferrites and ferrite-rich products of roasting of zinc blende. II. A. Simon and H. Hoppner (*Z. Elektrochem.*, 1943, 49, 296—305; cf. *ibid.*, 1940, 46, 458; B., 1944, I, 109; C., 1944, Part 3).—The products of roasting christophite ($4\text{ZnS} \cdot 2\text{FeS}$) at various temps. until no further SO_2 is evolved have been examined by microscopical, analytical, and X-ray methods. At low temp. $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , and ZnSO_4 are formed, the optimum temp. for production of the two first being 400° whilst max. yield of ZnSO_4 is obtained at 650° . At 700 — 1100° oxidation to $\text{ZnO} \cdot \text{Fe}_2\text{O}_3 + 3\text{ZnO}$ occurs. The max. content of material extractable with "Muspratt's solution" (71%) is attained after roasting at 600° , but this contains a considerable amount of SO_4^{2-} . At $>800^\circ$ most of the material extracted is free ZnO . After roasting at 1300° the ratio $\text{ZnO} : \text{Fe}_2\text{O}_3$ in the residue not extractable by this solution is 2.67 and suggests the existence of other Zn ferrites, but heating of a synthetic mixture of ZnO and Fe_2O_3 gave no evidence of the existence of such compounds.

J. W. S.

Removal of mercury from solutions of mercuric nitrate by mercuric sulphide. G. H. Spaulding and W. M. McNabb (*J. Franklin Inst.*, 1944, 237, 207—212).—The removal of Hg^{++} from dil. solutions of $\text{Hg}(\text{NO}_3)_2$ by freshly pptd. HgS follows the Freundlich adsorption isotherm. At higher concns. the isotherm is not followed, and there is a gradual change in the colour of the HgS from black to varying shades of grey until at $[\text{Hg}^{++}] > 4.7 \times 10^{-2} \text{M}$, a pure white ppt. remains. The formation of a substance with the possible formula $2\text{HgS} \cdot \text{Hg}(\text{NO}_3)_2$ is indicated.

C. R. H.

Mechanism of mercuric-chloro-oxalate complex formation in Eder's solution. M. C. Chen and C. J. Hsiao (*J. Chinese Chem. Soc.*, 1943, 10, 154—166).—Assuming an equilibrium between HgCl_2 , HgCl_3^+ , HgCl_4^{2-} , $\text{Hg}_2\text{Cl}_6^{2-}$, and HgCl_4^{2-} with HgCl_2 and $\text{C}_2\text{O}_4^{2-}$ in Eder's solution (cf. A., 1933, 1118), the concn. of the complex $\text{HgCl}_2 \cdot (\text{C}_2\text{O}_4)_2^{2-}$ (I) has been determined by a partition method. The results of Roseveare (A., 1930, 1135) are found to agree with a first-order decomp. of (I) and not of $\text{HgCl}_2 \cdot (\text{C}_2\text{O}_4)_2^{2-}$.

J. H. BA.

Interaction of boron fluoride with aluminium, silicon, and titanium oxides, and with silicates. Possible use of this reaction for opening up aluminosilicates for preparation of materials for the manufacture of aluminium. P. Baumgarten and W. Bruns (*Ber.*, 1941, 74, [B], 1232—1236).—The reaction, $\text{Al}_2\text{O}_3 + 3\text{BF}_3 \rightarrow (\text{BOF})_3 + 2\text{AlF}_3$, is quant. at 450° . The reverse reaction, $2\text{AlF}_3 + \text{B}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{BF}_3$, occurs at $\sim 800^\circ$ if an excess of AlF_3 is used but is not quant. owing to removal of B_2O_3 as $(\text{BOF})_3$. At 450° (not 350°), the reaction, $3\text{SiO}_2 + 6\text{BF}_3 \rightarrow 3\text{SiF}_4 + 2(\text{BOF})_3$, occurs, both products volatilising. TiO_2 reacts similarly but more slowly. Silicates are also attacked by BF_3 at 450 — 700° ; the Si is removed as SiF_4 , the Al becomes AlF_3 , the BF_3 is removed as $(\text{BOF})_3$, alkaline earths and Mg become fluorides, alkalis become fluoroborates (which at $>500^\circ$ yield fluorides and BF_3), and Fe remains as Fe_2O_3 ; after treatment with H_2O and conc. HCl , the AlF_3 can be used in the cryolite process for prep. of Al. By suitable recovery processes, a cyclic system can be set up.

R. S. C.

Rare earths. L. Separation of erbium from yttrium by fractional precipitation of the ferrocyanides. T. Moeller and H. E. Kremers (*J. Amer. Chem. Soc.*, 1944, 66, 307).—Details of the ferrocyanide procedure are given. Its success depends on complete removal of Fe.

W. R. A.

Metal carbonyls. XLVI. Osmium carbonyls. W. Hieber and H. Stallmann (*Z. Elektrochem.*, 1943, 49, 288—292).—The action of CO under pressure on Os halides in presence of Cu or Ag yields Os carbonyls. Max. yield is obtained with the oxyiodide (from OsO_4 and conc. HI) which when heated at 150° and 200 atm. CO pressure yields a mixture of carbonyls and $[\text{Os}(\text{CO})_2\text{I}]_2$. Carbonyls are also produced on heating OsO_4 at 150 — 200° in CO at >50 atm. and can be separated by fractional distillation. The main product is the yellow pseudo-hexagonal *diosmium nonacarbonyl*, $\text{Os}_2(\text{CO})_9$. The more volatile fraction contains the colourless liquid *Os pentacarbonyl*, $\text{Os}(\text{CO})_5$, m.p. -15° . The most volatile material contains traces of *Os carbonyl hydride*, $\text{OsH}_2(\text{CO})_4$, but no $\text{Os}(\text{CO})_4$ could be detected.

J. W. S.

XI.—GEOCHEMISTRY.

Cause of the increase in salinity of Barcelona's water supply. C. Chorower (*Anal. Fis. Quím.*, 1942, 38, 43—70).—Coincident with the exploitation of the Suria potash beds and the flow thence of saline effluent into the River Cardener over the period 1926—36, the H_2O supply of Barcelona contained excessive amounts of K^+ , Br^- , and Cl^- . This salinity could not be due to sea- H_2O as the SO_4^{2-} content of the supply remained normal.

F. R. G.

Limnological studies in Connecticut. VII. Critical examination of the supposed relationship between phytoplankton periodicity and chemical changes in lake water. G. E. Hutchinson (*Ecology*, 1944, 25, 3—26).—The spring appearance of *Dinobryon divergens* is correlated with a rise in the $\text{NO}_3^- : \text{PO}_4^{3-}$ ratio but is independent of

the concn. of sol. silicate. The appearance of *Asterionella formosa* does not appear to depend on the content of inorg. nutrients whilst *Anabaena circinalis* and *Fragilaria crotonensis* appear late when inorg. nutrients are at a low level, the former being favoured when NO_3^- is especially low. N fixation by *Anabaena* results in a more favourable habitat for *Fragilaria* as the *Anabaena* declines.

L. G. G. W.

Limnological observations on three lakes in eastern Vilas Co., Wisconsin. T. H. Flanigan (*Trans. Wisconsin Acad. Sci.*, 1942, 34, 167—174).—Temp., transparency, pH, free and combined CO_2 , and dissolved O_2 are recorded for the Crampton, Merrill, and Wood lakes. Benthos and plankton contents are high in Crampton and Wood lakes.

L. S. T.

Generation of magma by frictional heat. J. S. DeLury (*Amer. J. Sci.*, 1944, 242, 113—129).—An hypothesis to explain the origin of magmas within the earth's crust by reference to mechanical sources of heat is advanced.

L. S. T.

Paragenesis of the ore of the Normetal mine, Abitibi Co., Quebec. H. M. Putman (*Econ. Geol.*, 1943, 38, 313—322).

L. S. T.

Layered or banded chromite at Campo Formoso, Baía, Brazil. W. D. Johnston, jun., and H. C. A. de Souza (*Econ. Geol.*, 1943, 38, 287—297).—Chromite (I) at Campo Formoso occurs in layers alternating with layers of serpentine derived from olivine (II). The layered rocks may have been formed by the settling of alternate showers of (I) and (II) crystals on the floor of a magma chamber. Chemical analyses [R. E. Stevens] of (I) concentrates are given.

L. S. T.

Manganese oxide minerals: preliminary report. M. Fleischer and W. E. Richmond (*Econ. Geol.*, 1943, 38, 269—286).—X-Ray powder photographs, supplemented by chemical tests, provide the best means for identifying these minerals. X-Ray photographs, X-ray data, and physical properties are given for the commoner minerals and for those for which new data have been obtained. Formulae, and rules of nomenclature, are suggested.

L. S. T.

Gold ores of the Little Long Lac Area, Ontario. H. S. Armstrong (*Econ. Geol.*, 1943, 38, 204—252).—General geology, the nature of the ore bodies, and the mineral paragenesis of the various mines are described. The ore deposits of this area belong to Lindgren's upper hypothermal, or lower mesothermal, zone. Possible sources of the ore-depositing solutions are discussed.

L. S. T.

Chemical limestone in Central Pennsylvania. G. M. Kay (*Econ. Geol.*, 1943, 38, 188—203).—Deposits of high-grade limestone, particularly that of the Valentine member of the Curtin formation, are described. Chemical analyses of Valentine limestones are given.

L. S. T.

Post-mine leaching of galena and marmatite at Broken Hill. F. L. Stillwell and A. B. Edwards (*Econ. Geol.*, 1943, 38, 253—254).— Cl^- may be present in the underground waters of the North Broken Hill mine in sufficient concn. to cause reversal in the relative solubility of PbS and ZnS .

L. S. T.

Rare element prospecting in pegmatites. T. T. Quirke and H. E. Kremers (*Econ. Geol.*, 1943, 38, 173—186).—Certain chemical and mineralogical associations of the elements are proposed as a guide to the location of deposits of rare minerals in pegmatites. Lepidolite is a test mineral for the rare alkalis in pegmatites, ilmenite is a test mineral for V in magnetite, high-temp. epidotes are test minerals for the rare earths, titanite is probably a test mineral for Nb and Ta and apatite for the rare earths. Titaniferous magnetites should be examined for V as coulsonite.

L. S. T.

Effect of heat-treatment on magnetic properties of iron- and manganese-bearing minerals. G. G. Bring (*Jernkont. Ann.*, 1943, 127, 447—490; *Bull. Iron Steel Inst.*, 1944, No. 96, 37A).—The minerals studied were kriebelite (I) from Tuna Hästberg, Bastkärn, and Stollberg, grunerite (II) from Bastkärn, granite (III), "grona mineral" (IV) (a green, partly converted pyroxene) from Tuna Hästberg, and dolomite (V) from Tuna Hästberg and Klackberg. (I) and (II) became more magnetic and had increased remanence after being heated for 2 hr. at 800 — 900° . (I) from all localities and (II) are relatively strongly ferromagnetic. (III) and (IV) are paramagnetic after heating and no coercive force could be detected even after heating up to 900° with C. The only change in (V) from Tuna Hästberg was that the Mn content was increased by heating to 900° owing to expulsion of CO_2 . When Klackberg (V), which is higher in Fe, was heated at $\sim 700^\circ$ its magnetic susceptibility was increased 3—5 times; after roasting at higher temp. the val. decreased almost to that at room temp., whilst after roasting with C it rose steadily over the whole temp. range, probably because of formation of magnetite. (I) and (II) are sufficiently magnetic to be easily attracted in powerful magnetic separators, or to be separated in an a.c. field. (III) and (V) could be treated in a.c. fields of the strength used in these tests. After heat-treatment (III) responded somewhat better in powerful magnetic separators. Untreated specular Fe ore from different districts responded only slightly in powerful d.c. magnetic separators but quite well in a.c. separators.

R. B. C.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A I—General, Physical, and Inorganic Chemistry.

AUGUST, 1944.

I.—SUB-ATOMICS.

Shell spectrum of HR 8731 in 1940, with an intercomparison of the spectra of several shells. R. B. Baldwin (*Astrophys. J.*, 1943, 97, 388—393).—Analysis of the 1940 shell spectrum of HR 8731, which resembles that of ζ Tauri in 1914, shows lines of H, O I, Mg I, Mg II, Si II, Ca I, Ca II, Ti II, Cr II, Fe I, Fe II, Sr II, Sc II, and Ni II. The shell spectra of γ Cassiopeiae, ζ Tauri, ϵ Capricorni, β Monocerotis, Pleione, HR 8731, and ψ Persei indicate decreasing excitation conditions in the shell. The cooler shells, in which shell absorption is weak, usually contain less material. E. R. R.

Five spectroscopic binaries. D. M. Popper (*Astrophys. J.*, 1943, 97, 394—411).—Spectroscopic observations on SX Aurigae, V Puppis, ζ Centauris, RY Scuti, and i Bootis B are recorded. E. R. R.

Spectra of U Geminorum type variable stars. C. T. Elvey and H. W. Babcock (*Astrophys. J.*, 1943, 97, 412—425).—From new spectrograms of 21 stars, a summary of the characteristics of the spectra of U Geminorum type variables at min. and max. light is obtained and presented. E. R. R.

Spectrum of Pleione. O. Struve and P. Swings (*Astrophys. J.*, 1943, 97, 426—442).—The spectrum of the shell has become stronger (since 1938) and resembles the metallic spectrum of α Cygni. Dilution effects show in the weakness of Mg II and Si II. Lines of ions having metastable lower levels have appeared: Ni II and Fe II in 1940, Ti II in 1941, and Mn II in 1942, which order is inconsistent with the ordinary theory of ionisation. Low central intensities of the cores of H lines are explained by reduced re-emission which is thrown back within the shell into the emerging beam of radiation. The metallic lines on the violet side of the Balmer limit are relatively strong on account of the transparency of the shell and the absence of Stark effect wings in the shell. E. R. R.

HD 15963, a new shell star. W. P. Bidelman (*Astrophys. J.*, 1943, 97, 452).—The spectrum shows the simultaneous presence of an α -Cygni-like spectrum and abnormally broad He I lines, $\lambda\lambda$ 4026 and 4009. The Balmer series is sharp and strong. Si II and Mg II lines are weaker than in α Cygni; the lines $\lambda\lambda$ 4121, 4144, and 4471 are present. New spectrograms confirm these observations and show lines of Fe II, Ti II, and Mg I. The star is considered to be a shell star. E. R. R.

Investigation of "Bremsstrahlung" by means of excited ^{115}In nuclei. M. I. Korsunski, A. K. Walther, A. V. Ivanov, S. I. Zipkin, and V. E. Ganenko (*J. Physics, U.R.S.S.*, 1943, 7, 129—137).—The excitation of metastable ^{115}In is used as an indicator of the "Bremsstrahlung" produced by bombarding thin Au leaf and thick Be sheet with electrons of energies 1.04—1.5 Me.v. The observed isochromates ($h\nu = 1070$ e.k.v.) agree with Bethe and Heitler's theory (A., 1934, 1150), but are at variance with the results of Collins *et al.* (cf. A., 1940, I, 5). The relative probability for the production of an X-ray quantum varies as the square of the at. no. H. J. W.

New light effect in chlorine under electrical discharge. I. Influence of different irradiations on the production of the phenomenon under constant electrical conditions. P. G. Deo (*Proc. Indian Acad. Sci.*, 1944, A, 19, 117—122).—Conductivity under electrical discharge in Cl_2 is instantaneously and reversibly reduced on irradiation with visible light. The effect increases with the ν and intensity of irradiation under const. electrical conditions. L. J. J.

Calculation of the temperature of the electric arc, and problem of stability of the arc column. R. Mannkopff (*Z. Physik*, 1943, 120, 228—251).—An approximation method is used to calculate the radial variation of temp. in the arc column. The conductivity per cm., the ionisation potential of the gas, the column diameter, gas pressure, and edge temp. are parameters, and the thermal conductivity of the gas and the no. of carriers of charge as a function of temp. must be known. The calculation is applied to the arc in air. The temp. along the axis is $\sim 7000^\circ\text{K}$. Results for the outer zone could not be expected to agree with experiment as the effects of chemical reaction between N_2 and O_2 are not taken into account in the calculation. A. J. M.

Secondary electrons from photo-electric semi-conductors. H. Wolff (*Ann. Physik*, 1941, [v], 39, 591—603).—The emission from 161 K (A., I, 1)

various modifications of Se, and from Se photo-cells of known relative thickness of covering electrode, is investigated. The emission varies with the modification. Se sputtered from the vitreous state is deposited as the black form. Increase of thickness of the covering electrode gives a steady transition from the Se curve to the Au curve. No connexion between photo-electric properties and emission or velocity distribution is traced. Cd selenide phosphors are also investigated. Although the films varied considerably in properties they behaved in an identical manner on electron bombardment. Experiments with materials, some of which had been heated to redness and the others not, show that the heating has more effect on the emission power than has the addition of Cu. All the Cd selenide films show similar velocity distribution of the secondary electrons. A. J. M.

Spatial periodic distributions of freely falling ions and electrons. W. O. Schumann (*Z. Physik*, 1943, 121, 629—646).—Mathematical. Field-strength distribution curves for a variety of cases in which ions and electrons enter a vacuum space from opposite sides are computed. Periodic variations in space are possible in specified conditions. L. J. J.

Decay of ion concentration and electron temperature in the extinction of low-pressure discharges. G. Mierdel (*Z. Physik*, 1943, 121, 574—585).—Measurements of the ion concn. and electron temp. in a Hg plasma immediately following extinction, in a cylindrical tube, show quant. agreement with the diffusion theory of the column at pressures < 10 m-torr. At higher pressures vol. recombination takes place. The electron temp. falls very rapidly to $\sim 2000^\circ\text{K}$. and then much more slowly. The electrons are energised by the remaining metastable Hg atoms at this stage. The yield of collisions of the second kind is 1.8×10^{-3} . The dynamic component of the probe current expected from the growth of the Langmuir layer is not observed. L. J. J.

Significance of ionic diffusion for the structure of the ionosphere. E. Bagge (*Physikal. Z.*, 1943, 44, 163—166).—A differential equation for the diffusion of ions at great heights in the atm. is derived. It shows that if the diffusion effect is taken into account, the decrease of ionic density at the edge of the atm. is \propto no. of neutral gas atoms. The ionic density is 10^{-3} — 10^{-6} of the particle density of the corresponding gas. A. J. M.

Activation of a palladium surface by the glow discharge. R. Ulbrich (*Z. Physik*, 1943, 121, 361—376).—The surface of Pd is considerably activated by the glow discharge in H_2 or A. Both Pd wire and the compact metal become saturated with mol. H_2 at 30—130 torr after treatment with the glow discharge. The increase of electrical resistance and the absorption velocity were determined at various times. The curves consist of three parts: (1) a linear portion, (2) a second linear portion, making a smaller angle with the time axis than the first, and (3) a curve which approaches the saturation val. asymptotically. The two linear portions correspond to the concn. range in which solid compounds of Pd and H₂ exist, whilst the asymptotic portion corresponds to the dissolution of the gas in the metal. An electrode system composed of a Pd tube and a Ni cylinder shows a much greater polarity effect after treatment of the Pd cathode with the glow discharge. There appears to be an increased transmission of positive particles under the action of the electric field from a heated Pd tube through which A is passing, and this would explain the polarity effect. A. J. M.

Negative ions in Braun tubes and their connexion with oxide cathode mechanism. H. Schaefer and W. Walcher (*Z. Physik*, 1943, 121, 679—701).—Mass-spectroscopic investigation of the negative emission from oxide cathodes shows prevalence of H^- , CH^- , OH^- , O_2^- , and Cl^- ions, together with 11 weaker ionic species. All the ions found originate in the cathode except OH^- , which can also originate in the gas space by impact of H_2O on the cathode. The connexion between O_2^- and electron emission from the cathode shows activation of the latter to arise from Ba^+ ions leaving their regular lattice places and being adsorbed at electron-emitting points of disturbance. L. J. J.

Applications of incandescent anodes to mass-spectroscopic isotope separation. W. Walcher (*Z. Physik*, 1943, 121, 604—613).—The use of Kunsman-Koch electrodes of alkali chlorides supported on 16

W as ion sources for mass spectroscopy succeeds with the alkali metals, In, Ga, and Tl, but not with, e.g., alkaline-earth metals. The yield of alkali anodes of this type is nearly 100% of the alkali metal adsorbed on the inner W surface, and is independent of the emission current (up to 0.7 ma. for a Rb anode). An In anode gives only ~5% yield of ions. L. J. J.

Nuclear photo-effect in beryllium. F. G. Houtermans and (Frl.) I. Bartz (*Physikal. Z.*, 1943, **44**, 167—176).—The neutron efficiency of the (γ , n) process for Be with γ -rays from Ra-(B + C) is compared with the efficiency of a (Ra- α + Be) source by the method of Amaldi and Fermi. The yield of the γ -source per cm. thickness of the Be layer is $5.46 \pm 0.3\%$ of the yield of the comparison α -source of the same γ -equiv. Assuming that the most prolific of the (Rn- α + Be) sources emits 22,000 neutrons per m-curie per sec., and the no. of effective γ -quanta is 0.296 per disintegration, the mean effective cross-section of Be for the nuclear photo-effect with γ -rays from Ra-(B + C) is $(8.8 \pm 1.0) \times 10^{-28}$ sq. cm. These results are compared with those of other workers. A. J. M.

Energies and masses of nuclear fission particles obtained by bombardment of uranium with neutrons. W. Jentschke (*Z. Physik*, 1943, **120**, 165—184).—A U foil was bombarded with (Rn Be) neutrons, and the masses and energies of the fission products were investigated. Earlier experiments with thermal neutrons have been repeated; there is considerable analogy between the results with thermal and with fast neutrons. In the fission of the ^{235}U nucleus, the mass of the lighter product is 79—114, and of the heavier 125—160, with max. frequencies at 97 and 142. The fission products are, therefore, not equally massive when neutrons of ~10 Me.v. are used. The vals. obtained when fast neutrons are used are not so certain. With fast neutrons the mean total energy of the fission particles is 163 Me.v., and with thermal neutrons it is 160 Me.v. Experiments with Th, in the form of a thin layer on a thicker substrate, give 150 Me.v. for the mean total energy, and 141 and 92 for the masses of the most frequently occurring products. A. J. M.

Nuclear disintegration and heavy particles in cosmic rays. I. Heavy particles in cosmic rays as a consequence of nuclear disintegrations. II. Mechanism of collision and vaporisation processes. E. Bagge (*Ann. Physik*, 1941, [v], **39**, 512—534, 535—552).—I. The curve of frequency of occurrence of nuclear disintegration and of heavy particles with height follows almost the same course as that of the large Hoffmann collisions and cascade electrons. It is therefore concluded that the nuclear disintegration particles are released by light quanta or by charged particles of the soft component of cosmic rays. The mean energy of the radiation causing nuclear disintegration is calc. to be $>10^{10}$ e.v. A necessary consequence of the nuclear transmutation process is the occurrence of individual protons and neutrons in cosmic rays; the frequency of their occurrence agrees with the extent of nuclear transmutation. The energy spectrum of the proton paths is obtained and compared with experiment.

II. To explain the experimental energy distribution it is necessary to suppose that the primary process in collision consists of the collision of a no. of heavy particles, in many cases at least three. A formula for the velocity distribution of the emitted vaporisation protons and neutrons which takes into account the cooling effect on the nucleus of the emitting process is deduced. Comparison with experiment indicates that larger portions of the nucleus must be broken away in the vaporisation process. A. J. M.

Cosmic rays. W. F. G. Swann (*J. Franklin Inst.*, 1943, **236**, 521—540).—A popular-style lecture-survey of the discovery, properties, and theory of cosmic rays. N. M. B.

Separation of electronic and non-electronic components of cosmic radiation. H. J. Bhabha (*Proc. Indian Acad. Sci.*, 1944, **A**, **19**, 23—36).—Results obtained when the soft component of cosmic radiation is removed by absorption in a dense material must be interpreted with caution, as the exclusion of the soft component is \ll has been supposed. The behaviour of the soft component in passing through a slab of dense material is discussed on the basis of the cascade theory, and a formula for the depth of penetration of a cascade as a function of the energy of the primary electrons is obtained by the use of calculations due to Bhabha and Chakrabarty (*A.*, 1942, **I**, 350; 1943, **I**, 215). A simple formula for the end of a shower is also given. Fluctuation is important in determining the ability of an electron to operate two counters separated by a given thickness of absorber, and increases the no. of such electrons tenfold for thick absorbers. Formulae are given for the no. of electrons entering an absorber, and resulting in one or more particles emerging from the other side. A new experimental arrangement is described which makes more effective use of the cascade process for separating electrons from the penetrating radiation. It was devised especially for measuring the penetrating radiation in stratosphere balloon flights, the mass of absorber being kept as low as possible. It is also useful for studying the range spectrum of cosmic ray mesons. (*Cf. C.*, 1944, Part 3.) A. J. M.

Theory of the particle of spin 3/2. V. Ginzburg (*J. Physics*, U.R.S.S., 1943, **7**, 115—128).—A relativistic theory in spinor-vector form. H. J. W.

Quantum theory of radiation damping. E. Gora (*Z. Physik*, 1943, **120**, 121—147). A. J. M.

Stochastic problems in physics and astronomy. S. Chandrasekhar (*Rev. Mod. Physics*, 1943, **15**, 1—89).—A comprehensive review in which fundamental probability methods applied to physical and astronomical problems are considered. The problem of random flights is developed from the simple one-dimensional problem. The theory of the Brownian motion of a free particle, and of a free particle in a field of force, is considered. Smoluchowski's conception of probability after-effects is examined, and its application to colloid statistics is dealt with. The reversibility of thermodynamically irreversible processes, and the range of validity of the second law of thermodynamics, are also considered. Probability methods in stellar dynamics are reviewed. A. J. M.

II.—MOLECULAR STRUCTURE.

Shifts in the absorption spectra of mononuclear aromatic compounds. O. Schmidt (*Ber.*, 1941, **74**, [B], 987—1001).—Extinction curves in the near ultra-violet are determined for C_6Me_6 and C_6Et_6 in cyclohexane. Comparison with other alkyl-substituted benzenes shows an increasing shift of the band towards the red with increasing size of the substituent group. This is explained by the cylindrical electron box model of the C_6H_6 mol., in which decreases in the box radius (by substitution) are shown to alter the electronic levels in such a way as to result in a shift towards the red. The difference between the spectra of C_6H_6 liquid and vapour is accounted for in the same way. Shifts are observed in the spectra of C_6H_5 , PhCl , and C_6Et_6 in CHCl_3 solution, by addition of SnCl_4 , C_6Me_6 , and C_6Et_6 give yellow solutions in liquid SO_2 , SO_2Cl_2 , SnCl_4 , SOCl_2 , oleum, and ClSO_3H . These observations, and colour formations of hydrocarbons with other compounds of strong electron affinity, arise from an increase in the length of the electron box due to axial addition of the compounds. J. H. BA.

Absorption spectra of nitrophenols in liquid ammonia. N. Dichno and A. Schattenstein (*Acta Physicochim. U.R.S.S.*, 1942, **17**, 230—236).—The absorption spectra of *o*-, *m*-, and *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{OH}$, 2 : 4 : 1- and 2 : 6 : 1- $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{OH}$, and picric acid in liquid NH_3 were determined in the range 2500—6000 Å. Nitrophenoxide ions are formed in liquid NH_3 , and the log ϵ - λ curves are therefore similar to those obtained in aq. NaOH; the curves for liquid NH_3 , however, are shifted towards longer λ . Experiments with 3 : 5 : 1- $\text{C}_6\text{H}_3(\text{NO}_2)_3\text{CO}_2\text{H}$ in liquid NH_3 confirm that the effect of salt addition is the larger, the smaller is the radius and the larger is the charge of the ions of the salt. J. F. H.

Absorption spectra of 1 : 2-benzanthracene and of some methoxy-derivatives. E. R. Holiday (*Cancer Res.*, 1943, **3**, 689—690).—An absorption curve (2300—4000 Å.) is given for 4'-methoxy-1 : 2-benzanthracene in $n\text{-C}_8\text{H}_{18}$, and the λ of absorption max. are compared with those for 1 : 2-benzanthracene (I), 9 : 10-dimethyl-1 : 2-benzanthracene, and a methylated metabolite from mice injected with (I) (*cf. A.*, 1944, III, 489). A. J. E. W.

Effects of environment and aggregation on absorption spectra of dyes. S. E. Sheppard (*Rev. Mod. Physics*, 1942, **14**, 410).—Errata (*cf. A.*, 1943, **I**, 192).

Ultra-violet absorption spectra of protein solutions. R. N. Jones and H. J. Crech (*J. Opt. Soc. Amer.*, 1943, **33**, 209—218).—Analyses of conjugated proteins, formed by the interaction of serum-proteins with the carbimides of certain polynuclear aromatic hydrocarbons, are described. The no. of hydrocarbon groups introduced into each protein mol. can be determined provided the hydrocarbon chromophore has absorption max. at $\lambda > 3250$ Å. B. S. C.

Fluorescence spectrum of uranyl fluoride. D. D. Pant and N. D. Sakhwaker (*Proc. Indian Acad. Sci.*, 1944, **A**, **19**, 135—140).—The fluorescence spectrum of solid UO_2F_2 has been investigated at liquid air temp., and the 17 sharp and discrete bands have been classified as five groups and five series. The bands, interpreted using the three UO_2^{++} ν , are due to transitions from the excited (0,0,0)' and (0,1,0)' states to various vibrational levels of the ground state. W. R. A.

Spectrofluorescence, with special reference to sugars. S. J. Lewis (*J.S.C.I.*, 1944, **63**, 157—160).—When a fluorescent substance is illuminated by a spectrum, the curve of the intensity of the degraded light at successive λ is an expression of the chemical nature of the substance. It discriminates not only between associated substances, e.g., mannitol and glucose, but also between a pure substance and the same substance when embodying a very small proportion of a minor compound, e.g., sucrose alone and when medicated with 1% of raffinose. The method is applicable to both solids and solutions.

Distribution of radiant energy in fluorescent spectra of atabrin and other acridine derivatives. T. C. Butler (*J. Pharm. Exp. Ther.*, 1944, **80**, 70—73).—Data of absorption and fluorescent spectra of atabrin dissolved in C_6H_6 , $m/15\text{-PO}_4'''$ buffer at pH 8 and 5.9, $iso\text{-C}_6\text{H}_{11}\text{OH}$, or lactic acid, 2 : 5-dichloro-7-methoxyacridine in $iso\text{-C}_6\text{H}_{11}\text{OH}$, 2-chloro-5-amino-7-methoxyacridine hydrochloride

in H_2O , and 2-chloro-7-methoxy-5-acridone in C_6H_6 are given. For all these compounds, the fluorescent spectra cover a wider band of longer λ than do the absorption spectra. The λ exciting max. fluorescence corresponds with the λ at which the absorption bands fade out. G. P.

Nature of spectral diffuse emission of solutions of rare-earth salts. A. A. Schischlovski (*Acta Physicochim. U.R.S.S.*, 1942, 17, 135—151).—The absorption spectra of aq. solutions of Ce^{+++} salts and of cryst. solutions in transparent La salts have approx. the same structure. The photoluminescence of Ce^{+++} salts is generally unaffected by the surrounding medium. No quenching agents were found. The absorption of Ce^{+++} solutions is not affected by the presence of alkaline-earth chlorides, bromides, or iodides, or of HCl or HNO_3 . From these results and theoretical considerations it is concluded that the Ce^{+++} ion, and not a complex, is the "centre" in the photoluminescence of Ce^{+++} salts. The mechanism of absorption and emission of other extreme ions of the rare-earth group is discussed in relation to the structure of their $4f^n$ shell. J. F. H.

Effect of temperature on the intensities of Raman lines. III. Liquids. K. Venkateswarlu (*Proc. Indian Acad. Sci.*, 1944, A, 19, 111—116).—In typical liquids (e.g., CCl_4 , C_6H_6 , Bu^+OH , and PhCl) the Stokes lines (except 215 cm^{-1} of CCl_4) decrease in intensity with increase of temp., whereas the anti-Stokes lines increase. The latter effect is $<$ that expected. The Stokes:anti-Stokes ratio agrees with that calc., but Stokes intensity does not agree with calc. vals. (Cf. A., 1942, I, 387.) L. J. J.

Raman effect in relation to crystal structure: sodium nitrate. B. S. R. Rao (*Proc. Indian Acad. Sci.*, 1944, A, 19, 93—99).—To account for the observed Raman and infra-red ν of cryst. NaNO_3 , force consts. 5.42×10^5 , 1.78×10^6 , 0.64×10^5 , and 4.40×10^6 , the same as those calc. for the free ion, and 0.03×10^5 , 0.35×10^6 , and 0.07×10^6 , referring to interionic forces, are adopted. Calc. Raman and infra-red ν are 87, 190, 766, 1069, 1362, and 60, 71, 157, 292, 439, 716, 843, 1411 cm^{-1} , respectively. The ν of the total symmetric oscillation 1048 in the free ion increases to 1069 cm^{-1} in the crystal. Two "lattice lines" at frequencies 190 and 87 cm^{-1} are predicted by the calculation, and five different ν shifts in the infra-red spectrum. L. J. J.

Raman effect and hydrogen bonds. IX. Solutions of salicylic acid and aspirin. G. V. L. N. Murty and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1944, A, 19, 17—20).—The Raman spectrum of salicylic acid in dioxan (I) and in C_6H_6 has been investigated. Results indicate that in (I) unimol. chelate structures with the solvent predominate. In C_6H_6 some unimol. chelate structures exist, but the majority consists of dimers of indefinite structure, presumably some kind of open structure. The Raman spectrum of acetylsalicylic acid in (I) indicates the existence of chelate structures. A. J. M.

Rotation of molecules in the crystal lattice and light scattering. E. Gross and A. Raskin (*Acta Physicochim. U.R.S.S.*, 1942, 17, 127—134).—Some crystals exhibit anomalies in sp. heat, dielectric const., etc. in the temp. region immediately below the m.p. This behaviour is generally accompanied by an enantiotropic transition to a higher-temp. form with greater symmetry. Such crystals are intermediate between true crystals and liquids and hence are called "quasi-liquid crystals". The diffusion spectra of some examples of such substances [CBr_4 , cyclohexanol, camphor, borneol, camphene (I), and C_2Cl_6] were examined around the Rayleigh line at temp. between the transition temp. and the m.p.; the low- ν diffusion spectra of the liquids were also examined. None of the crystals examined showed any low- ν lines of noticeable intensity. (I) and C_2Cl_6 showed a distinct background extending 20—25 cm^{-1} away from the Rayleigh line. The results do not enable a choice to be made between the Pauling-Fowler theory of complete rotation and the Frenkel theory of "orientation fusion" for such substances. J. F. H.

Longitudinal scattering of infra-red rays and the mol. wt. of high- and low-molecular substances. W. W. Lepeschkin (*Kolloid-Z.*, 1943, 105, 205—208).—The rule that the longitudinal scattering of infra-red rays (Plotnikov effect) is \propto cube root of the mol. wt. of the scattering substance is accurate for lower-mol. homologues. For other low-mol. substances the scattering is dependent not only on mol. wt. but also on mol. structure. The presence of OH, and particularly of CO_2H , favours scattering. The ratio of the scattering in a high-mol. substance to that in a low-mol. substance which contains OH and CO_2H is $<$ the ratio of the cube roots of the mol. wts., and the structure factor is >1 . For sucrose the factor is 1.38, for citric acid it is 1.43, and for a degradation product of gelatin, 1.6. As a general rule, in such cases, the ratio is more nearly that of the fourth root of the mol. wts. It is possible to determine the mol. wts. of the lower-mol. degradation products of proteins by applying this rule. A. J. M.

Effect of water vapour, gases, and vacuum on the crystal photo-[electric] effect in semi-conductors. M. Ögder (*Rev. Fac. Sci. Istanbul*, 1943, 8, A 23—35).—The influence of H_2O vapour on the photo-electric effect for proustite (two varieties), pyrrargyrite

(one variety), and cuprite (three varieties) has been examined; in all cases there is an increase in the photo-electric effect. In a vac. there is a min. in the e.m.f. and current-time graphs for two varieties of cuprite and for the third a sinking to a const. low val. For proustite and pyrrargyrite there is a variation in e.m.f. and current but no min. Dry, electrolytically produced O_2 and H_2 have no effect on proustite after keeping in a vac. The variation of e.m.f. and current with intensity of illumination for this crystal shows that at high intensities it is possible to measure the current but not the potential. Some other secondary phenomena are described. The general pretreatment of crystals was washing with a brush moistened with EtOH. Dipolar mols. are adsorbed on the crystal surface in the liquid state, forming a double layer, the conductivity of which is $<$ that of the crystal surface, so that the potential and current rise. The min. is caused by the increase in conductivity due to a decrease of adsorbed mols. on evacuation, followed by a decrease in conductivity due to the disappearance of O_2 . These results, taken with those of Brauer and Dubar (A., 1936, 1055), prove the correctness of Dember's model of a photo-cell (A., 1932, 8).

J. O'M.B.
Breakdown and time-lag of dielectric materials. Breakdown of liquid carbon tetrachloride. S. S. Attwood and W. H. Bixby (*J. Franklin Inst.*, 1943, 235, 259—272).—Theories and formulae are discussed. Experimental data for CCl_4 indicate that modern theories may be applicable to a wide range of dielectrics if their mol. constitution is ionic, and that the technically important time-lag follows a simple rule in its dependence on over-voltage. N. M. B.

Interferometry. I. (A) C. V. Raman. (B) L. B. Tuckerman. (C) S. Tolansky (*Phil. Mag.*, 1944, [vii], 35, 210—213).—(A) A priority claim (cf. Tolansky, *ibid.*, 1943, [vii], 34, 555).

(B) Attention is directed to work by Pohl (*Physikal. Z.*, 1940, 41, 498).

(C) A reply.

H. J. W.

Origin and complications of electric double refraction and of electric dichroism in dilute dispersed systems. W. Heller (*Rev. Mod. Physics*, 1942, 14, 390—409).—A general survey of the possible causes of double refraction in steady and alternating fields. Complications may be due to orientation by convection or sedimentation, to orientation or deformation in an inhomogeneous field, and to the competition between intrinsic and "form" double refraction for anisometric particles. Four types of electric dichroism are noted—two due to absorption and two to scattering or reflexion.

H. J. W.

Migration double refraction of fibre molecules in an electric field. W. Kuhn and H. Kuhn (*Helv. Chim. Acta*, 1944, 27, 493—499).—Methylcellulose degraded to an ~ 60 -fold polymer and oxidised by I to methylcellulosemonocarboxylic acid shows strong double refraction when its aq. solutions are placed in electric fields of 450—1200 v. per cm. The double refraction const. is 1.1×10^{-8} , in qual. accord with the val. deduced from consideration of the orientation of the mols. in the electric field. J. W. S.

Hydrogen bond. C. E. Kendall (*Chem. and Ind.*, 1944, 211).—The effect of H bonding on η is considered (cf. Friend, A., 1944, I, 149). The variation of η with mol. wt. for compounds in which the intermol. forces are (a) van der Waals forces, (b) dipole attractions and van der Waals forces, (c) H bonds, dipole attractions, and van der Waals forces, is shown graphically. Compounds of class (c) have higher η than the others. The aliphatic acids have lower η than the corresponding alcohols, since the latter form transient groups of mols. linked by H bonds, whilst the acids tend to form dimers in which the H bonds are stabilised by resonance. Comparison of the η of *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Cl-OH}$ (4.20, 16.7, and 23.0 centipoises, respectively, at 20°) indicates that H bonding occurs in these compounds, and that it is intramol. in the case of the *o*-compound, and intermol. in the others. A. J. M.

Systematics of states of aggregation. G. F. Huttig (*Kolloid-Z.*, 1943, 104, 161—167).—The conceptions of mol. mobility, degree of ordering, and degree of dispersion are used as parameters in the discussion of a state of aggregation. A diagram is given showing how the various states of aggregation differ with regard to these parameters. A. J. M.

Temperature variation of surface tension and the molecular diameters of water and benzene. A. Espurz (*Anal. Fis. Quim.*, 1942, 38, 303—315).—From vals. of γ for H_2O and C_6H_6 it is calc. by the Ramsay-Shields formula that the degrees of association are 3.20 and 1, respectively. The "active surface tension" γ_a arising from the kinetic energy is related to the surface tension γ_0 at 0° K. by $\gamma_a = \gamma_0(V_0/V)^{2/3} - \gamma$ and should replace γ in the formula of Mokrouskin (A., 1924, ii, 820). The calc. val. of the mol. diameter of C_6H_6 is $>$ that given by Sirk's formula. F. R. G.

Measurement of surface tension by means of sessile drops. [Surface tension of water.] H. J. Taylor and J. Alexander (*Proc. Indian Acad. Sci.*, 1944, A, 19, 149—157).— γ for H_2O against saturated air is 72.70 ± 0.07 and 71.56 ± 0.07 dynes per cm. at 20° and 27.7°, in good agreement with recorded vals. (Cf. C., 1944, Part 3.) W. R. A.

Parachors of *cis*- and *trans*-decahydronaphthalene. F. H. Lee (*J. Chinese Chem. Soc.*, 1943, 10, 16—18).—The parachors of *cis*- and *trans*-decahydronaphthalene, calc. from the data of Seycr and Davenport (A., 1941, I, 458), are 366.0 and 370.1, whereas the calc. val. is 368.0 for both isomerides. J. W. S.

III.—CRYSTAL STRUCTURE.

Fundamentals of crystal physics. (Sir) C. V. Raman (*Current Sci.*, 1943, 12, 342—344).—An address.

Low angle X-ray scattering from chrysotiles. I. Fankuchen and M. Schneider (*J. Amer. Chem. Soc.*, 1944, 66, 500—501).—Both wide- and low-angle X-ray diffraction of four chrysotiles are studied. Wide-angle scattering is similar in each case. Two lines are visible in each low-angle diagram, the ratios of the Bragg spacings being $\sqrt{3}$, suggesting a parallel fibrous structure. Diameters of the fibrils have been calc., and it is suggested that differences in mechanical properties can be correlated with different fibre diameters.

W. R. A.

Influence of crystal size on the absorption factor as applied to Debye-Scherrer diffraction patterns. A. Taylor (*Phil. Mag.*, 1944, [vii], 35, 215—229).—The absorption factor τ for a spherical crystal is calc. from the tabulated factors for cylindrical crystals due to Bradley (A., 1935, 1306). A table of τ is given for various reflecting angles and crystal sizes. The application of these results to a cylindrical powder specimen is discussed, and the effects of crystallite aggregation, size, and dilution in the embedding matrix are considered.

H. J. W.

Geometry of spherical packing. I, II. R. Straubel (*Kolloid-Z.*, 1943, 104, 167—180; 105, 227—241).—I. Mathematical. A no. of cases of spherical packing are considered.

II. The geometry of spherical packing of systems with up to 12 elements is worked out. The stability of each arrangement is discussed.

A. J. M.

Various types of disturbances in crystal lattices and their influence on chemical reactions and surface activity. J. A. Hedvall (*Chalmers Tekn. Högskol. Handl.*, 1942, No. 4, 25 pp.).—Theories of imperfections in crystal lattices are reviewed. Reversible imperfections are considered, and the application of the Schottky-Wagner theory of faulty arrangement to the formation of solid solutions is discussed. In some cases of reactions between solids, e.g., Ag_2HgI_4 from AgI and HgI_2 , the process can be followed kinetically. Theory and experiment agree closely in the case of the formation of Cu_2O . The effect of irreversible imperfections is also considered, especially in the case of the reactivity of Fe_2O_3 with CaO . The possibility of changing the surface activity of solids by disturbances less violent than the production of real imperfections, e.g., by magnetic, electrical, and photochemical effects, is discussed. The kinetics of the decomp. of HCO_2H in contact with a Pd-Co catalyst have been investigated, and it is found that there is a marked change of velocity in the neighbourhood of the Curie point. There are 5—10 times as many active centres when the catalyst is in the paramagnetic state compared with the ferromagnetic state. There is a discontinuity in the velocity of dissolution of Rochelle salt at the electric Curie point. The effect of light on surfaces is dealt with. Experiments with CdS and phenolphthalein (I) show that the quantity of (I) adsorbed on CdS is smaller in light than in darkness. The difference of activity of different surfaces of the same crystal is also evident in photochemical processes. The layer-latticed CdI_2 , when irradiated with short-ultra-violet in the presence of traces of H_2O , was attacked only on the "prism" faces, which were blackened, while the ionic surfaces were unaffected. O_2 inhibited the effect. The effect is also observed with the crystal form of CdBr_2 which is similar to CdI_2 , but not with the other modification.

A. J. M.

Diffraction of X-rays by liquid elements. N. S. Gingrich (*Rev. Mod. Physics*, 1943, 15, 90—110).—The diffraction of X-rays by 23 liquid elements has been investigated by various workers, and the results are here reviewed. The intensity and distribution curves are given for 16 elements. On the basis of assumed models for the liquid state, ideal distribution curves can be constructed. Comparison of these curves with the observed data makes it possible to obtain interat. potentials and certain physical properties of the liquid. The curves also indicate the mol. state of the liquid.

A. J. M.

Electron microscope photographs of the lamellar structure of magnesium hydroxide. T. Marx and G. Wehner (*Kolloid-Z.*, 1943, 105, 226—227).—X-Ray experiments (Fricke *et al.*, A., 1937, I, 83) indicate that $\text{Mg}(\text{OH})_2$ has a layer lattice, the thickness of the lamellae being ~ 100 Å. This has been confirmed by the investigation of commercial $\text{Mg}(\text{OH})_2$ with the electron microscope; the thickness of the lamellae is 20—100 Å. It is possible that this is not the original form of the $\text{Mg}(\text{OH})_2$ crystal, as change of structure may occur under the conditions of high vac. and temp. used with the electron microscope. The same type of structure was observed with MgO obtained by heating the same $\text{Mg}(\text{OH})_2$.

A. J. M.

Investigation by electron diffraction of the structures of halogen derivatives of tin, arsenic, and nitrogen. H. A. Skinner and L. E.

Sutton (*Trans. Faraday Soc.*, 1944, 40, 164—184).—The following are the lengths, in Å., of the central atom-halogen links, determined from electron-diffraction patterns of the vapours, in the compounds indicated: SnMe_2Cl 2.37 ± 0.03 , SnMe_2Cl_2 2.34 ± 0.03 , SnMeCl_2 2.32 ± 0.03 , SnMe_2Br 2.49 ± 0.03 , SnMe_2Br_2 2.48 ± 0.02 , SnMeBr_2 2.45 ± 0.02 , SnMe_2I 2.72 ± 0.03 , SnMe_2I_2 2.69 ± 0.03 , SnMeI_2 2.68 ± 0.02 , AsMe_2Cl 2.18 ± 0.04 , AsMe_2Br 2.34 ± 0.04 , AsMe_2I 2.52 ± 0.03 (cf. 1.77 ± 0.02 for NMe_2Cl and 1.74 ± 0.02 for NMeCl_2). These and other data indicate that, in general, such links become progressively shorter as the no. of halogen atoms displacing H or Me on the central atom increases. This behaviour is in accordance with the theory that bond contractions are a function of differences of electronegativity, but not with one that ignores the effects of charge redistribution arising from multiple bonding.

F. L. U.

Magnetic investigations of organic substances. XXI, XXII.—See A., 1944, II, 189.

Scattering of light by single crystals. Intensity measurements. S. Bhagavantam and K. Venkateswarlu (*Proc. Indian Acad. Sci.*, 1944, A, 19, 108—110).—Relative intensities of Rayleigh and Raman lines in calcite and quartz crystals are determined for different orientations, CCl_4 being used as intermediate standard. The Rayleigh intensity is 2—7 times that of the principal Raman line.

L. J. J.

Statistical theory of the brittle strength of real crystals. J. I. Frenkel and T. A. Kontorova (*J. Physics, U.R.S.S.*, 1943, 7, 108—114).—The strength of a crystal is assumed to be determined by the most "dangerous" inhomogeneity present. The strength of a crystal therefore depends on its vol., just as in the "weak link" theory the strength of a chain depends on its length. A statistical treatment of brittle strength is given.

H. J. W.

Correlation of solution potentials with orientations of single crystals of high-purity aluminium.—See A., 1944, I, 178.

Elasticity, creep, and recovery of acetate and viscose rayon yarns.—See B., 1944, II, 133.

Isomorphism and polymorphism of barbituric acid derivatives. (Fr.) M. Brandstatter (*Z. physikal. Chem.*, 1942, A, 191, 227—240).—The phase behaviour of binary mixtures of some 40 derivatives of barbituric acid was investigated by the contact method of Kofler (C., 1944, Part 3). Examples of Roozeboom's types I, III, IV, and V, as well as mixed types, are given.

J. F. H.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Theory of the intermediate state of superconductors. L. Landau (*J. Physics, U.R.S.S.*, 1943, 7, 99—107).—The intermediate state is assumed to be laminar, alternate laminae being normal. The laminae split up into fringes near the surface of the superconductor. This leads to an explanation of the hysteresis in the transition to the intermediate state. The behaviour of a superconductor containing a narrow slit transverse to the magnetic field is investigated.

H. J. W.

Higher paraffin hydrocarbons. Correlation of physical properties. A. W. Francis (*Ind. Eng. Chem.*, 1944, 36, 256—260).— d_4^{20} and n_D^{20} of *n*-paraffins and of paraffins of structures CHRR' , CHETRR' , $\text{Pr}^b[\text{CH}_2]_n\text{Pr}^b$, and $(\text{CHRR}')_2$ can be expressed $A - B/x$, where x is the total no. of C atoms (< 11) and A and B are const. for each structural series but vary with the series. For other paraffins these properties can be calc. by adding suitable increments dependent on the mode of building their structures from those of lower paraffins. The b.p. of branched-chain paraffins are correlated similarly but show wider discrepancies.

J. W. S.

Specific heat of zirconium dioxide at low temperatures. K. K. Kelley (*Ind. Eng. Chem.*, 1944, 36, 377).—Fused ZrO_2 (purity 99.14%; SiO_2 0.30, TiO_2 0.20, CaO 0.07%) has C_p (corr. for impurities) 1.473 at 54.3° K., rising to 13.25 at 295.0° K. (27 vals. determined at intermediate temp.); hence $S = 12.03 \pm 0.08$, and $\Delta G = -244.2$ kg.-cal., at 298.16° K.

M. H. M. A.

Determination of the thermal constants of samples of activated charcoal and silica gel. L. K. Simonova (*J. Appl. Chem. Russ.*, 1943, 16, 87—94).—Measurements were made on air-dried industrial adsorbents comprising three samples of activated bone-C and one of SiO_2 gel. Diffusivity vals. (sq. m. per hr. $\times 10^{-4}$) were at 0° 5.41—8.19, at 20° 5.91—9.08, and at 70° 7.87—13.34. Powdering of the samples increased these vals. by $\sim 11\%$. Thermal conductivity (kg.-cal. per m. per hr. per degree) was in the range (0°) 0.08—0.17, (20°) 0.09—0.21, and (70°) 0.12—0.24. The average increase on powdering was 35.9%. Sp. heat (kg.-cal. per kg. per degree) varied from 0.294 to 0.332; the influence of temp. was negligible but the sp. heat was decreased $\sim 2\%$ by powdering.

V. B.

Mechanism of the dependence of the thermal conductivity on pressure in gases. I. Ethyl chloride. K. Schafer and O. R. Foz (*Anal. Fis. Quim.*, 1942, 38, 316—340).—Vals. of k for EtCl show a variation with p > that required by Maxwell's theory. This is attributed to the formation of double mols. for $p > 50$ mm.; the

expression for the second virial coeff. is shown to be $B_1 - RT/k_p$, where B_1 is due to double mols. F. R. G.

Some problems involving line sources in conduction of heat. J. E. Jaeger (*Phil. Mag.*, 1944, [vii], 35, 169—179).—The temp. due to an instantaneous line source parallel to the axis of a solid cylinder embedded in a solid medium of different thermal const. is determined. The problem of a line source of given strength moving with a const. angular velocity around the surface of a solid cylinder is also solved. This solution is applied to the practical problem of the grindstone used in wood-pulping. H. J. W.

Thermodynamic properties of light hydrocarbons. D. E. Holcomb (*Ind. Eng. Chem.*, 1944, 36, 384).—Enthalpy charts given previously (A., 1942, I, 321) are corr. J. W.

Differential equations of wave propagation in gases. K. Bechert (*Ann. Physik*, 1941, [v], 39, 357—372).—Mathematical. L. J. J.

Variation of the viscosity of gases and vapours with temperature. W. Licht, jun., and D. G. Stechert (*J. Physical Chem.*, 1944, 48, 23—47).—Equations relating η and temp. of gases are reviewed. With the exception of H_2 and He for which Trautz's equation is equally satisfactory, Sutherland's equation has been shown to be the most reliable. A universal η equation, which is independent of the substance and requires knowledge only of crit. temp. and pressure and mol. wt., has been derived. A nomograph for determining η from this equation is reproduced. C. R. H.

Calculation of most probable concentration in diffusion theory. E. M. Galvez Laguarda (*Anal. Fis. Quim.*, 1942, 38, 102—104).—The most probable val. of the concn. of a diffused phase is expressed mathematically in terms of the initial condition of the system and the Brownian effect. The formula can be applied to the calculation of the rate of propagation of matter, heat, light, and electricity.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Structure of water in aqueous solutions. D. D. Eley (*Trans. Faraday Soc.*, 1944, 40, 184—194).—The two-stage process, (1) creation of a cavity in the H_2O , (2) insertion of a gas mol. in the cavity, is used in a discussion of the energy and entropy of dissolution of inert gases. Previous work (cf. A., 1938, I, 519; 1939, I, 607) is extended by presenting a mol. theory for the low energy of cavity formation and by showing that the smallness of this energy term is due to a polarisation of the H_2O mols. in the region of the cavity that persists when an inert gas enters the cavity. There is evidence that, whilst an inert gas atom can occupy only a restricted no. of sites in H_2O , ions can exchange with any H_2O mol. in the solution, considered as a quasi-lattice. Existing theories of the partial molal heat capacities of ions in aq. solutions fail to account for the opposite effect on this property of increasing ionic radius shown by inert gases on the one hand and by ions on the other. An explanation based on a long-range polarisation extending far beyond the first hydration shell is offered. F. L. U.

Apparent ionic volume in infinitely dilute solutions. F. H. Lee (*J. Chinese Chem. Soc.*, 1942, 9, 46—53).—In alkali metal halide solutions the apparent vol. V of the ion pairs at infinite dilution is related to the spherical vol. of the ions in the cryst. state (v_e and v_a) by $V = A(v_e + v_a) - B$, where A and B are const. dependent on temp. with the vals. 1.87 and 20.7 cu. Å., respectively, at 25°. The vals. of V for Na halides are low, indicating that the Na^+ ion has an abnormally small vol. in solution. The relation is explained by supposing v_e and v_a to be determined by the effective ionic vol. due to its kinetic effect and by the electrostriction of a unimol. layer of H_2O around the ion. J. W. S.

Osmotic pressures for mixed solvents. F. T. Wall (*J. Amer. Chem. Soc.*, 1944, 66, 446—449).—Mathematical. The osmotic pressure, π , of solutions in mixed solvents has been derived thermodynamically. Measured vals. of π have definite significance only when the solutions on either side of the membrane have different compositions, subject to certain relationships. Van't Hoff's equation holds true for infinitely dil. solutions. With conc. solutions, complications are to be expected in the determination of π , especially with dynamic methods. W. R. A.

Cryoscopy of isanic acid. Y. Doucet and M. Fauve (*Compt. rend.*, 1942, 215, 533—534).—The cryoscopic const. in $AcOH$ is 3.72 and in C_2H_5 5.12. The mol. wt. of the acid is 274, and the structure $CH_2[CH[CH_2]_4C_2C_2C_2C[CH_2]_4CO_2H$. N. M. B.

Critical graphical methods for calculating isotonic concentrations and freezing points of aqueous solutions.—See A., 1944, III, 497.

Fine structure of glasses. Change of fine structure in system P_2O_5-ZnO .—See B., 1944, I, 235.

Density, thixotropy, and setting of silver amalgams.—See B., 1944, I, 243.

Volume relations in alloys in the heterogeneous liquid-solid region. I. F. Sauerwald (*Metallwirts.*, 1941, 20, 405—408; cf. A., 1944, I,

102).—Existing data are reviewed and discussed with particular reference to the systems Fe-C, Cu-Sn, Cu-Zn, and Cu-Al. C. E. H.

Structure of hard metal alloys. W. Dawidl and J. Hinnüber (*Kolloid-Z.*, 1943, 104, 233—236).—The hardness of metal alloys composed of WC and ~6% of a metal of lower m.p. (Co) can be explained as due to the formation of a WC skeleton. The strength of this skeleton is revealed by treating sintered plates of the alloy with HCl, which leaves an almost complete skeleton of WC crystals. If the sintered plate contains >10% Co, it disintegrates when treated with HCl. The variation of mechanical strength of pure WC, and of alloys with 6 and 11% Co, with sintering temp. has been determined, and the results agree with the WC skeleton theory. A. J. M.

Physico-chemical study of phases having the nickel arsenide structure in the systems iron-antimony, cobalt-antimony, and nickel-antimony. N. V. Ageev and E. S. Makarov (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 87—98).—Ni-Sb alloys containing 41—56 at.-% of Sb are studied. From micro-sections, the lattice spacings a and c , electrical resistance r , and its temp. coeff. α , it is concluded that the γ phase exists between 46.4 and 54.4 at.-% of Sb. At 50 at.-% of Sb r has a min., and α a max., and at 54.4% r has a max. and α a min. The hardness h (Shore) has a min. at 50% of Sb. The γ phase of Co-Sb alloys (42—54 at.-% of Sb) lies between 43.4 and 49.6% of Sb. Within the γ phase r and h decrease when the % of Sb increases. This phase is a solid solution of Co in the "apparent" compound CoSb. The ϵ phase of Fe-Sb alloys (35—51 at.-% of Sb) lies between 42 and 48% of Sb. Data on r and α are incomplete because of the brittleness of this phase, and h decreases when the % of Sb increases. In the series Ni-Co-Fe r increases and α decreases. The a spacing increases in the order Co < Ni < Fe, and c in the order Fe < Ni < Co. The strength of the chemical bond increases in the order FeSb < CoSb < NiSb. J. B.

Gas solubility and partial pressure. Nomograph for correlation of data. D. F. Othmer and R. F. Benenati (*Ind. Eng. Chem.*, 1944, 36, 375—377).—Nomograms are given for obtaining the partial pressure at various temp. for CO_2 in H_2O , C_2H_6 , and aq. $Na_2CO_3 + NaHCO_3$; HCl, NH_3 , SO_2 , and Cl_2 in H_2O ; SO_3 in H_2SO_4 . J. W.

Solubility of aluminium bromide in n -butane. J. D. Heldman and C. D. Thurmond (*J. Amer. Chem. Soc.*, 1944, 66, 427—431).—Measurement of the solubility of $AlBr_3$ in n - C_4H_{10} from 28.3° to 97.5° (m.p. of $AlBr_3$) reveals no evidence for a phase transformation in $AlBr_3$ at ~70°. The system is regular in the Hildebrand sense. The solubility of $AlBr_3$ in 18 other solvents is briefly discussed. W. R. A.

Mechanism of solvent action. A. K. Doolittle (*Ind. Eng. Chem.*, 1944, 36, 239—248).—The processes operating during the dissolution of macromol. substances are assumed to involve solvation-desolvation equilibria between the solute and solvent and aggregation-disaggregation equilibria between solute mols. For solvent mixtures comprising an active solvent mixed with a diluent liquid the min. mol. concn. of solvent ("threshold concn.") required to initiate dissolution decreases to a const. min. val. on ascending a homologous series of solvents. This val. ("class threshold concn.") is independent of the diluent, provided this is a true non-solvent. In certain cases it is possible to pass out of the solvent region at the low mol. wt. end of a series, and it is always possible to do so at the high mol. wt. end since the mol. concn. of pure compound decreases with increasing mol. wt. For solutions of const. solute concn. $\log \eta - A + B/n$ (η = viscosity, n = concn. of solvent liquid, A and B are const.), except near the threshold concn., where $\log \eta$ rises rapidly with decreasing n , approaching ∞ as n approaches the threshold concn. The application of the author's theory to the mechanisms of film formation and plasticisation are discussed. J. W. S.

Penetration of hydrogen in monocrystalline and polycrystalline iron. A. Portevin, G. Chaudron, and L. Moreau (*Compt. rend.*, 1942, 215, 361—363; cf. A., 1943, I, 59).—The expulsion of adsorbed H, by heating in vac. at different temp., was investigated by microscopic examination and hardness tests after submitting the residual gas to ionic bombardment following each heating. Results are tabulated, and differences in the retention of the H in the lattice and in the intergranular joints and its expulsion for the two cryst. forms of Fe are discussed. N. M. B.

Occlusion of hydrocarbons by chabazite and analcite. R. M. Barrer and D. A. Ibbitson (*Trans. Faraday Soc.*, 1944, 40, 195—206).—Sorption equilibria between the zeolites and paraffin hydrocarbons up to C_8 have been studied at various temp. Isotherms and some isosteres are given. Sorption of CH_4 and C_2H_6 occurs very rapidly, and that of the higher members fairly rapidly only at or above 100°. Branched chains are not sorbed. Thermodynamic properties (ΔH , ΔA_0 , ΔS_0) of the solid solutions are obtained as functions of charge of gas, chain length, or temp. In both chabazite and active analcite the affinity of solutes for the lattice increases in the order He < H_2 < O_2 , A < N, CH_4 < C_2H_6 < C_3H_8 < n - C_4H_{10} . F. L. U.

Kinetics of formation of zeolitic solid solutions. R. M. Barrer and D. A. Ibbitson (*Trans. Faraday Soc.*, 1944, 40, 206—216; cf.

preceding abstract).—Solute are occluded in chabazite and active analcite at rates depending on their cross-sectional diameter (d). For $d > 4.0$ Å. (He, H₂, O₂, N₂, CH₄, C₂H₆) mols. are taken up by free diffusion down minute channels; for $d = 4.89$ (higher n -paraffins) the process is one of slow diffusion in which an energy of activation is needed; mols. with $d < 5.58$ Å. (isoparaffins and aromatic hydrocarbons) are totally excluded. With n -paraffins the rate decreases with increase in chain length, and with increase in the concn. of gas initially within the zeolite; it is also modified by the conditions of dehydration of the sorbent. The kinetics of sorption are those of a pure diffusion process, without any rate-determining phase boundary processes. The sorption rate increases exponentially with rise of temp., and apparent energies of activation are given for C₃H₈, n -C₄H₁₀, n -C₅H₁₂, and n -C₇H₁₆. F. L. U.

Effects of salts on the adsorption of erythrosin on silver halides. A. P. Tai and C. L. Chen (*J. Chinese Chem. Soc.*, 1943, 10, 22—29).—The effects of KCl, KBr, KI, and KCNS on the adsorption of erythrosin on AgBr, AgCNS, and AgCl are irregular and hence the adsorptions of the anions do not follow the Paneth-Fajans rule. The observations made are interpreted on the basis of pptn. of less sol. Ag halides, disruption of the crystal lattice of the ppt. through adsorption of larger anions, and the increased adsorption of K⁺ as compared with the Na⁺ present in the indicator. J. W. S.

Adsorption of thorium on tantalum.—See A., 1944, I, 138.

Adsorption of sodium alkyl sulphate by wool and other fibres.—See B., 1944, II, 160.

Adsorption from non-aqueous solutions. V. Aleixandre (*Anal. Fis. Quím.*, 1942, 38, 378—382).—AcOH adsorbed by kaolin from CS₂, CCl₄, C₆H₆, PhMe, MeOH, and EtOH decreases as the dipole moment increases and is approx. in accordance with Freundlich's equation. F. R. G.

Approximate relation between surface tension and concentration for regular solutions. M. Wales (*J. Chem. Physics*, 1944, 12, 135—142).—An equation for the variation of surface tension (γ) with concn. in regular solutions has been derived using Hildebrand's model and calculating the work per unit interfacial area required to separate a body of liquid reversibly into two infinitely removed parts, spherical symmetry in shape and mol. field of both components being assumed. The general equation is $\gamma = v_1\gamma_1 + v_2\gamma_2 + C v_1 v_2$, where v_1 and v_2 are vol. fractions and γ_1 and γ_2 are the respective vals. of γ for the pure components. C is a const. depending on other properties of the mixture under consideration, and equations relating C with these properties are derived. Its val. is generally $\leq 2\sqrt{(\gamma_1\gamma_2)}$. For ideal solutions $C = \gamma_1 + \gamma_2$ so that $\gamma = v_1\gamma_1 + v_2\gamma_2$. All recorded data for regular solutions quantitatively fit one or other of these equations with the exception of CS₂-C₆H₆; possible reasons for the non-uniformity of this system are discussed. C. R. H.

Surface activity. IX. Cryoscopy and surface activity in benzene solutions of aliphatic alcohols. X. Cryoscopy and surface activity in benzene solutions of fatty acids. A. Giacalone (*Gazzetta*, 1942, 72, 378—389, 429—439).—IX. F.p. measurements of C₆H₆ solutions of n -C₄H₉+1·OH ($x = 1-6$) are recorded and discussed in relation to the v.p. measurements of Butler *et al.* (*Trans. Faraday Soc.*, 1931, 27, 797). Depression of f.p. diminishes as mol. concn. of solute increases; contrary to experience in H₂O (A., 1940, I, 203), the diminution in depression is the greater the lower is the mol. wt. of the alcohol. From activity coeff. at infinite dilution the variations in mol. free energy for each additional CH₂ are calc. γ of MeOH, EtOH, and BuOH in C₆H₆ at 27° is recorded.

X. F.p. measurements of C₆H₆ solutions of n -C₂H_{2x+1}·CO₂H ($x = 0-8$) (and also of C₇H₁₅) are recorded. Again diminution in depression is the greater the lower is the mol. wt. of the acid. Variation in mol. free energy is greatest between AcOH and PrOH, and small and approx. const. between other adjacent pairs. Mol. free energy of dissolution decreases constantly in successive members. γ of AcOH, EtCO₂H, and PrCO₂H in C₆H₆ at 27° is recorded. E. W. W.

Rates of evaporation of water through compressed monolayers on water. I. Langmuir and V. J. Schaefer (*J. Franklin Inst.*, 1943, 235, 119—162).—A method is described for the determination of the rate of evaporation of H₂O from a clean surface and from one covered by a compressed monolayer. The rate of evaporation is measured by finding the increase in wt. of a vessel containing CaCl₂ placed at a known distance above the surface. Decrease of temp. of the surface due to evaporation, and increase of temp. of the CaCl₂ above it, effectively reduce convection. The rate of escape of mols. from the H₂O surface was decreased in the ratio of $\sim 10^4$ to 1 by the presence of a monolayer of cetyl alcohol. By analogy with Ohm's law, the evaporation resistance is defined by the equation, rate = driving force/resistance. The evaporation resistance (ω_r) of films increases rapidly with their surface pressure, and the increase is \gg can be accounted for by an energy barrier. ω_r of monolayers of highly purified fatty acids with 16, 18, 19, 20, 21, and 23 C atoms, and of C₂₀H₄₁·OH, have been determined and the effect of pH of the substrate and the presence of Ca and Ba salts has been studied. There is a linear relationship between surface pressure,

F , and $\log \omega_r$, represented by $\log_{10} \omega_r = -3.08 + 0.0425F + 0.122n$ (n = no. of C atoms in acid). Curves of F against a , the area per mol., are also given. Collapse pressures for the films are much higher for acids having an odd no. of C atoms. The F - ω_r curves show a hysteresis effect. Experiments were also carried out with mixtures of cholesterol and the C₂₃ acid, the results indicating that minute amounts of impurities can exert a great effect on ω_r . To investigate whether high ω_r depends on a strong localised compressive force at a definite level in the monolayer, experiments were carried out with mixtures of the C₂₁ acid and θ -dihydroxystearic acid (I). The presence of only 30% of the C₂₁ acid causes rapid collapse of a film of (I). The effects of thick layers of oil on rate of evaporation of H₂O have also been investigated. The results are discussed theoretically. A. J. M.

Surface phenomena in non-conducting liquids under the influence of electric discharges in gases. T. Rummel (*Kolloid-Z.*, 1941, 96, 340—347).—A thin layer of oil spread on the surface of a tube in series with a high-potential discharge forms into drops on the surface. Thicker layers in vessels form a variety of surface figures, the shapes depending on the viscosity and type of oil used. Mobile liquids, e.g., CCl₄, give foams under the same conditions. When liquid and gas layers are placed in parallel, as between plates partly filled with liquid, the angle of contact of the liquid becomes $> 90^\circ$ on application of the field, but falls below normal when discharge occurs. The phenomena are discussed in relation to the energy at the surfaces. J. H. BA.

Production of monodisperse substances. A. H. M. Andreasen (*Kolloid-Z.*, 1943, 104, 181—189).—The production of monodisperse BaSO₄ of grain size 3—0.3 μ . by condensation has been investigated. The effect of mixing solutions of SO₄²⁻ and Ba²⁺ in the presence of various substances was studied. It is possible to obtain monodisperse spherical particles of $\sim 3 \mu$. diameter if a substance which increases the solubility (HCl) is added before mixing the solutions. If a substance which decreases the solubility is added, the particles are smaller. Another method, in which the reaction employed took place slowly, and in which pptn. was therefore gradual, was also used. Thus, monodisperse Cu₂O was obtained by adding Fehling's solution in excess to a solution of a reducing sugar. Monodisperse HgI₂ and TlI were obtained by mixing solutions of the corresponding iodates with Na₂SO₃. A series of monodisperse products of BaSO₄ were obtained in the form of long rounded particles of 4—0.14 μ . diameter by mixing solutions of BaCl₂ and H₂O₂ with Na₂S₂O₃ and adding various quantities of normal Na citrate. A. J. M.

Influence of van der Waals forces on coagulation of aerosols. M. V. Tichomirov, N. N. Tunitzki, and J. B. Petrijanov (*Acta Physicochim. U.R.S.S.*, 1942, 17, 185—196).—An equation is deduced which shows that the rate of coagulation of an aerosol is determined uniquely by the mean vals. of R , $1/R$, and $1/R^2$, where R is the radius of the particles. On taking into account the interaction between the particles, i.e., the van der Waals forces, the coagulation const. is increased by a factor γ , which is independent of R but is determined by the const. in the van der Waals forces equation. Experiments with mists of mineral oil, tritoly phosphate, and H₂SO₄ give γ vals. of 1.25, 1.22, and 1.30, respectively. J. F. H.

Determination of size, shape, and anisotropy of submicroscopic particles (colloids and macromolecules) by means of double refraction and viscosity. H. A. Stuart (*Kolloid-Z.*, 1941, 96, 161—168).—The application of equations for viscosity, and electrical, magnetic, and streaming double refraction, to the determination of particle dimensions is discussed for different ranges of particle size. J. H. BA.

Structure of soap solutions. J. Stauff (*Kolloid-Z.*, 1941, 96, 244—251).—The theories of soap solution structure are reviewed and suggestions made about the micellar structure at various concns., which are supported by approx. energy calculations. J. H. BA.

Powder dispersoids and their derivatives. W. Ostwald (*Kolloid-Z.*, 1943, 104, 137—139).—A review. The characteristic properties of powders, and their importance in technology, are mentioned. The incoherent nature of powders and the methods of converting them into a coherent system are considered. Metal and C powders show a reversible change between coherence and incoherence. It is possible to make "solid" bodies from powders by the application of high pressures, and these substances have almost the same d as the compact material, but they differ considerably from the latter in physico-chemical properties. The hardness of a compressed powder may be $>$ that of the compact form obtained by fusion. A. J. M.

Elementary processes of fritting and sintering metal powders with special reference to the real structure of their surfaces. F. Sauerwald (*Kolloid-Z.*, 1943, 104, 144—160).—Methods of prep. of metallic powders are summarised. The nature of the free surface of metallic powders is considered, and two types of roughness are recognised, one, produced, e.g., by breaking, and visible under the optical or electron microscope, and the other at., being related to the fine structure of the surface. The vectorial nature of surface energy, and the variation of surface tension of different surfaces of a crystal, are considered. Other factors of importance in connexion with the surface are the velocity of its formation, and the presence of foreign

substances, especially O_2 . The internal surfaces of regular bodies are also considered. Cold pressing, hot pressing, fritting, and sintering are discussed. The effect of fritting and sintering processes on the properties of metals, particularly mechanical strength, is described. The strength is dependent on the temp. of sintering.

A. J. M.

Effect of the gaseous atmosphere on the chemical activity and surface properties of powders during their formation. J. A. Hedvall and A. Lundberg (*Kolloid-Z.*, 1943, **104**, 198—203).—The effect of heating powders (SiO_2 , Al_2O_3) in O_2 , N_2 , air, SO_2 , and SO_3 at various temp. on their surface properties has been investigated. The activating effect decreases at high temp., and the differences in activity between two different preps. of the same powder are very great, indicating that the effect is due to dissolution of the gas. Experiments with mixtures of CuO and SiO_2 indicate that it is not merely an adsorption layer. The activity varies with the gas pressure, and the variation of reactivity of heated powder mixtures according to the pretreatment they have received with gases is similar to the effect on recrystallisation.

A. J. M.

New methods of investigation of colloidal systems. D. Beischer (*Kolloid-Z.*, 1941, **96**, 127—135).—A review of the application of electron microscope and electron diffraction technique to the elucidation of colloidal structure.

J. H. BA.

Determination of the basic texture of gels by means of double refraction. W. J. Schmidt (*Kolloid-Z.*, 1941, **96**, 135—147).—The various ways in which double refraction may occur are discussed in relation to gel structure.

J. H. BA.

Systematics of gels. E. Manegold (*Kolloid-Z.*, 1941, **96**, 186—210).—The fine structures which may occur in gels are tabulated under the main headings of corpuscular, laminar, and fibrillar skeletons, and each is discussed in detail.

J. H. BA.

Fine structure of solids made up of particles of colloidal size and their physical and chemical properties. R. Fricke (*Kolloid-Z.*, 1941, **96**, 211—225).—A discussion of the surface energy of solids with reference to its dependence on the constitution and size of the crystals concerned, the origin of active spots, and specificity of chemical reactions at surfaces.

J. H. BA.

Nature of water film in plastic clay.—See B., 1944, I, 236.

Optical properties of gels. I. Thorium molybdate gels. II. Thorium arsenate gels. III. Silicic acid gels. M. Prasad and S. Guruswamy (*Proc. Indian Acad. Sci.*, 1944, **19**, A, 47—65, 66—76, 77—87).—I. The intensity and depolarisation factors of light scattered transversely by Th molybdate gels have been determined. The intensity was measured photoelectrically, and the depolarisation factors (ρ_v , ρ_h , ρ_u) by Cornu's method with a double-image prism and a Nicol. Comparison of light scattered at 45° and 135° shows that the size of the particles is $\sim 0.25 \lambda$ of the light used. The density scattering, I_D , and the anisotropy scattering, I_A , have been calc. separately, and their changes during gelation have been investigated. I_D increases during gel formation owing to increase in vol. and decrease in no. of particles. As this is analogous to coagulation it is inferred that gelation is a coagulation and a hydration phenomenon. In the early stages of gel formation I_A , I_D , but it decreases rapidly during gelation. There is no great difference in the final vols. of gel particles formed under different conditions. The Krishnan relation between ρ_v , ρ_h , and ρ_u holds for this gel (cf. A., 1935, 821).

II. Similar investigations were made with Th arsenate gels. The particle size is $\sim 0.25 \lambda$ of the light used. The intensity of scattered light, and ρ_v and ρ_u were found in one case to increase greatly even after the gel had set. The particles increase in size by ~ 25 times during gel formation, and this is largely independent of conditions of formation. Krishnan's formula applies reasonably well to this gel.

III. Similar investigations have been made with silicic acid gels. The size of the particles is of the same order as those of the other gels investigated. I_D increases during gel formation. I_A is small compared with I_D in the early stages of gel formation, but increases later, as the gel particles become more anisotropic. The particles increase in vol. 15-fold during gel formation, the increase being largely independent of conditions. Krishnan's formula holds fairly well for this gel.

A. J. M.

X-Ray investigation of the structure of soap solutions. H. Kiessig (*Kolloid-Z.*, 1941, **96**, 252—255).—X-Ray diagrams of Na oleate in H_2O show a well-defined long spacing (a) which decreases to that found in the solid soap with increase in concn. A more diffuse small spacing (b) of 4.4 \AA is independent of soap concn. This indicates soap micelles formed from double mols. which are extended lengthwise by the interposition of a H_2O layer between the polar groups. Addition of C_6H_6 to the aq. soap solution increases a but not b . The C_6H_6 is thus interposed between the non-polar groups of the double mols. in the micelle. Laurylpyridinium chloride gives sharp X-ray rings in aq. solution but not in EtOH. Preliminary experiments on an aq. polyethylene oxide derivative also show micelle formation, but the solutions have a smaller a than the solid.

J. H. BA.

Mechanical properties of soap solutions and their relation to structure. W. Philippoff (*Kolloid-Z.*, 1941, **96**, 255—259).—The η_{rel} -concn. curve for aq. K laurate shows a deviation from linearity at $\sim 1\%$ but in EtOH no such deviation occurs. The deviation varies with addition of KOH, being a min. at 0.6N-KOH. These solutions also show a strong temp.-dependence of η_{rel} , structural viscosity, streaming double refraction, and a less sharp X-ray picture. Addition of m -cresol to aq. Na oleate gives a max. in the concn. curve and a decrease in the long spacing in the X-ray picture, and the mixtures show structural viscosity. The micellar structure of soap solutions is discussed and a hexagonal micelle is proposed.

J. H. BA.

Effect of association and solvation on the structure of cellulose solutions. E. Steurer (*Kolloid-Z.*, 1941, **96**, 333—335).—The osmotic pressure of ethylcellulose (I) in 90% C_6H_6 —10% EtOH (II), $CHCl_3$, dioxan, C_6H_6 , and PhMe is measured. (II), $CHCl_3$, and dioxan give the same mol. wt. on extrapolation to zero concn., but C_6H_6 and PhMe give higher vals. tending to decrease with decrease in concn. beyond 1.5 g. per l. for PhMe. *cyclo*Hexane, 95% C_6H_6 —5% $COMe_2$, 70% C_6H_6 —30% C_6H_{14} , and m -xylene behave as C_6H_6 and PhMe. These increases decrease with increase in temp. and on addition of polar solvents, and are due to association of solute mols. in the non-polar solvents. A comparison of tetramethyl- and 2:3:6-trimethyl-methylglucoside and (I) shows an increase in association with the no. of OH groups in the mol. The temp.-dependence of the viscosity of (I) is greatest in non-polar solvents and is accounted for on the same basis.

J. H. BA.

Deformation and swelling mechanisms in cellulose gels. P. H. Hermans (*Kolloid-Z.*, 1941, **96**, 311—317).—The anisotropic swelling is measured at various degrees of extension for cellulose gels with varying degrees of initial swelling. The anisotropy increases more quickly with extension for the more swollen gels, but if the degree of extension is calc. on the initial and final dry states all samples show the same anisotropy at the same extension. The crystallinity increases on drying and extension. The structure of cellulose is discussed on the basis of these results.

J. H. BA.

Effect of traces of inorganic salts on the fall in viscosity of cellulose nitrate solution. J. S. Gourlay (*J.S.C.I.*, 1944, **63**, 123—124).—The rate of decrease in η of $COMe_2$ solutions of cellulose nitrate on ageing is increased if the solvent contains NaCl or $CaCl_2$; the initial η of the solution is also decreased.

Nitration of cellulose. I. Nitration in the vapour of nitric acid. G. L. Wilson and F. D. Miles (*Trans. Faraday Soc.*, 1944, **40**, 150—163).—The reaction of cellulose with HNO_3 vapour at 20° and 40° has been followed by suspending bundles of ramie from a quartz spring balance in a stream of the vapour at 4—16 mm. pressure, the extent of reaction and of adsorption being calc. from the observed increase in wt. and the chemical analysis of the product. Adsorption reaches a max. in ~ 3 hr., and the rate of nitration, the max. of which coincides with the adsorption max., is approx. \propto (amount of adsorbed HNO_3)². It is inferred that 2 mols. of HNO_3 are concerned in the conversion of each OH, thus: $OH + 2HNO_3 \rightarrow O \cdot NO_2 + HNO_3 \cdot H_2O$. The max. degree of nitration observed (1 week at 40°) was N 13.7%. Raising the temp. does not greatly increase the rate of nitration, since the resulting increase in the velocity coeff. is largely compensated by the decrease in adsorption. Fractional dissolution of some of the products in aq. $COMe_2$ showed them to be very inhomogeneous (e.g., 10.7 and 13.35% N for the extreme fractions) and to have abnormally low solubility. Adsorption of HNO_3 vapour on a highly nitrated specimen (N 13.7%) was measured at 20° and 40° , and the results could be fitted to the Langmuir equation. The calc. mol. heats of adsorption are 16.4 and 14.0 kg.-cal. at 10 and 20% adsorption.

F. L. U.

Association and solvation of cellulose acetate from dielectric measurements. H. Erbring and M. Takei (*Kolloid-Z.*, 1941, **96**, 336—340).—The polarisation of cellulose acetate (I) in dioxan shows a decrease with increasing concn. which is attributed to association of the solute. The polarisation decreases with increase of % MeOH in MeOH— $COMe_2$ mixtures, but is independent of the concn. of (I) in these mixtures. This shows lack of association and a const. solvation which is independent of concn. Using the extrapolated val. at infinite dilution for the polarisation in dioxan, solvation nos. for (I) in various solvents are calc.

J. H. BA.

Relationship between viscosity and strength of gel of pectin solutions. L. Malsch (*Biochem. Z.*, 1941, **308**, 283—296).—Aq. pectin solutions, after treatment with NaCl, behave as homopolymers, and obey Staudinger's viscosity law. The viscosity-concn. ratio is \propto strength of gel. The isolation of purified pectin preps. following hydrolysis of the raw material by HCl at pH 0.7 for 48 hr. at 40° is described. The average galacturonic acid content is 65—75%. The OMe content averages 5—7%, but is reduced to 1—3% by prolonged acid hydrolysis (7 days).

P. G. M.

Structural changes in gels on freezing. H. Ullrich (*Kolloid-Z.*, 1941, **96**, 348—353).—The pH of gelatin solutions in citrate buffers, originally at pH 1.7—7.7, after freezing show a shift towards the isoelectric point, $\log \Delta pH$ being $\propto \log [\text{gelatin}]$. The softening

points show an increase after freezing. The increase is a max. at the isoelectric point for solutions of 2–4% and 7–10% gelatin, is a min. for 4–7%, and is independent of pH for 4% and 7% solutions. The frozen gels show double refraction which increases with temp. and concn. [With agar solutions $\log \Delta p H \propto 1/\log [\text{agar}]$, and no change is evident in citrate buffer at pH 5.8. There is no change in softening point. Addition of salts increases coacervation and double refraction. In mixed agar-gelatin solutions coacervation occurs at 2°. The observations are discussed in relation to the changes occurring in plants on freezing. J. H. BA.

Light scattering experiments with high polymer solutions. P. M. Doty, B. H. Zimm, and H. Mark (*J. Chem. Physics*, 1944, 12, 144–145).—From an equation for the turbidity of a colourless binary mixture due to fluctuations in d and concn., an expression is derived which shows that a plot of $H(g_2/r_2)$ against g_2 should give at low concns. a straight line having an intercept of $1/M_2$ [r_2 = turbidity of solution less turbidity of solvent, g_2 = g. of solute per c.c., M_2 = mol. wt. of solute, and H is a function of wave-length, n , and concn.]. Turbidity data for PhMe and COMeEt solutions of polystyrene fractions show this linear relation. C. R. H.

Longitudinal scattering of infra-red rays, Tyndall effect, and mol. wt. of proteins.—See A., 1944, III, 497.

Theory of molecular size distribution and gel formation in branched polymers. II. General cross linking. W. H. Stockmayer (*J. Chem. Physics*, 1944, 12, 125–131; cf. A., 1943, I, 126).—A statistical calculation of the gel point and of the mol. size distribution is made for cross-linked high polymers of arbitrary initial size distribution. The wt.-average polymerisation degree of the cross-linked polymer depends only on the wt.-average polymerisation degree of the initial polymer and the degree of cross-linking. The treatment is not generally applicable to cases of copolymerisation of a vinyl derivative with sufficient quantity of a divinyl derivative since polymerisation and cross-linking are concomitant rather than consecutive, but restricted applications are possible, and these are discussed. C. R. H.

Electrical double refraction and electrical dichroism in dilute dispersed systems.—See A., 1944, I, 166.

Anomalous viscosity and flow-birefringence of protein solutions. III. Changes in these properties of myosin solutions in relation to adenosine triphosphate and muscular contraction.—See A., 1944, III, 498.

Influence of ions on the settling of a suspension of powdered quartz. V. Romanovsky (*Compt. rend.*, 1942, 215, 531–533).—Measurements are tabulated for various cations, and, for a given cation, for various anions. Sediments are characterised by the index ϵ = vol. of liquid/vol. of solid. Results show that ϵ is very small with twice-distilled H_2O but increases sharply with tap water; for a given anion, ϵ increases with the at. wt. of the metal cation, and also with the valency of the anion; for a given cation, ϵ is independent of the associated anion; for particles of 7–20 μ , ϵ tends to decrease as the size of the particles increases. N. M. B.

VI.—KINETIC THEORY. THERMODYNAMICS.

Calculation of the composition of equilibrium gas mixtures at high pressures. A. B. Brodski (*Acta Physicochim. U.R.S.S.*, 1942, 17, 228–229).—The equation given previously (A., 1944, I, 103) for the activity coeff. of a gas is a mathematical expression of the results of Newton and Dodge (A., 1935, 823). Calc. vals. for the yields of NH_3 from N_2 and H_2 at 300–600 atm. agree well with observed vals. J. F. H.

Alkalinity of concentrated solutions of alkali hydroxides. G. Schwarzenbach and R. Sulzberger (*Helv. Chim. Acta*, 1944, 27, 348–362).—The method of Hammett and Deyrup (A., 1932, 921) has been applied to determine the alkalinity of 0.1–19.5N-NaOH and 0.1–15.2N-KOH at 20°. Nine indicators dissolved in various org. solvents were used and the ratio of the concns. ($[S]/[HS]$) of their colour forms in the solvent in equilibrium with the alkali solutions was determined by extinction coeff. measurements. From the results the pH vals. of the solutions have been derived by application of the relation $(pH)_1 - (pH)_2 = (\log [S]/[HS])_1 - (\log [S]/[HS])_2$. J. W. S.

Acid-base studies in the gaseous phase. I. Precise dissociation measurements. H. C. Brown, M. D. Taylor, and M. Gerstein. **II. Anomalous base strength of the methylamines. A new manifestation of steric strain.** H. C. Brown, H. Bartholomay, jun., and M. D. Taylor (*J. Amer. Chem. Soc.*, 1944, 66, 431–435, 435–442).—I. An apparatus for determining the degree of dissociation of AB additive compounds in the gas phase has been developed. Samples of A and B are placed in separate tensimeters, with bulbs of equal vol. (within 0.05%), and the amount of substance is adjusted until the pressures, measured by Hg manometers, are identical (within 0.02 mm.). The more volatile substance is then condensed by liquid N_2 into the other tensimeter, and the gas pressure of the additive compound, thus synthesised, measured at $\sim 5^\circ$ intervals from $\sim 10^\circ$ above the saturation point, and checked with decreasing temp.

The purity of the additive compound is accurately determined by measuring the v.p. at 0°. The accuracy of the method has been examined, using NMe_3 , BMe_3 as additive compound. K_p and ΔH of dissociation can be determined to 2% and 0.1%. Measurements at ~ 25 and ~ 10 mm. initial pressure show that deviations from the gas laws do not introduce considerable errors.

II. Highly purified samples of the additive compounds of BMe_3 with NH_3 (I), NH_4Me (II), $NHMe_2$ (III), and NMe_3 (IV) have been prepared, and their m.p., v.p., and dissociation in the gas phase measured. M.p. are: (I) 73.2–73.7°, (II) 26.9–27.2°, (III) 35.0–35.5°, and (IV) 128°. V.p., in the temp. ranges indicated, are: (I) (20.0–59.7°), $\log p = -(3095/T) + 11.229$; (II) (34.7–93.1°), $\log p = -(2829/T) + 9.611$; (III) (45.7–80.0°), $\log p = -(2902/T) + 9.880$; (IV) (29.8–65.1°), $\log p = -(3467/T) + 11.949$. Vals. of $\log K_p$, in the temp. ranges indicated, and ΔH of dissociation (in kg.-cal. per mol.), are: (I) $-(3007/T) + 8.723$ (54.8–130.0°), 13.75 ± 0.3 ; (II) $-(3856/T) + 8.880$ (85.4–139.9°), 17.64 ± 0.2 ; (III) $-(4211/T) + 9.595$ (85.1–125.6°), 19.26 ± 0.2 ; and (IV) $-(3852/T) + 9.998$ (65.8–111.3°), 17.62 ± 0.2 . The relative affinity of the methylamines for BMe_3 is identical with their affinity for H^+ , the base strength increasing from (I) to (III), but decreasing considerably in (IV). To account for this, two strain effects are postulated: an "F-strain," depending on the steric requirements of both base and acid, and a "B-strain," depending on the steric properties of base alone. B-strain is predominant in BMe_3-NH_2Me compounds. W. R. A.

Effect of metallic ammine salts on pH of phosphate buffer solutions. L. H. Cobb and J. S. Anderson (*Trans. Faraday Soc.*, 1944, 40, 145–150).—Addition of $[Co(NH_3)_6]Cl_3$, $[Coen_3]Cl_3$, $[Pt(NH_3)_4]Cl_2$, and of $[Ir(NH_3)_6]Cl_3$ to phosphate buffers, M./15 with respect to PO_4^{3-} and varying in pH from 7.17 to 5.29, causes a decrease in pH that calc. from the change in ionic strength. The effect appears to be a sp. property of the added cation. Measurements at 20° are recorded for varying concns. of the ammine salts up to 0.08M. Over a fairly wide range the pH of the solutions is a linear function of $\log [\text{ammine}]$. F. L. U.

Peculiarities of H and OH ions. P. Jolibois (*Compt. rend.*, 1942, 215, 344–345).—Electrolysis phenomena of H_2O and of strong acids can be explained by the theory of Arrhenius with the help of the hypothesis of hydration of ions. N. M. B.

Diffusion and dialysis coefficients of positively charged elementary ions. H. Spandau (*Z. physikal. Chem.*, 1943, A, 192, 211–228).—A crit. analysis of measurements of dialysis coeffs. (λ) with Cellophane and Cuprophane membranes shows that no conclusions can be drawn from them about the extent of ionic hydration. Determinations of λ with "Cellafilters" indicate that the ratio of λ to the diffusion coeff. (D) increases slightly with increasing charge on the ion. The product λD (M = mol. wt.) for different ions is not const., as claimed by von Koss. From the relation $D \sqrt{M}$ = const. the hydration for various ions is calc. The results agree with other vals. The relation $D = hu/n$ (u = mobility, n = valency, h const.) is shown to hold with a few exceptions. J. H. BA.

Ionic dissociation frequency of complex binary ions in aqueous solution. R. Daudel (*Compt. rend.*, 1942, 215, 301–303).—Investigations for a no. of ions are reported and discussed. N. M. B.

Chemistry in anhydrous hydrogen cyanide. G. Jander and G. Scholz (*Z. physikal. Chem.*, 1943, A, 192, 163–210).—The cryoscopic const. of HCN is determined and the cryoscopic method used to show that amines, e.g., NEt_3 , form cyanides in HCN which ionise in the solvent, but that H_2SO_4 , SO_3 , and $CH_3Cl \cdot CO_2H$ are undissociated. By analogy with H_2O the CN group is basic, and neutralisation reactions, e.g., $KCN + H_2SO_4$, are followed by salt pptn. and conductometric and potentiometric measurements, which indicate in some cases the formation of acid salts. The ionic product $[H^+][CN^-]$ is determined potentiometrically. Solvolysis, e.g., $Ag_2SO_4 + 2HCN \rightarrow 2AgCN + H_2SO_4$, and amphoteric behaviour (with Fe salts) are also observed. The reaction of SO_3 with HCN is of the first order, and the product is a tribasic acid $(OH)_3S(CN)_3$. J. H. BA.

Electrochemical determination of activity coefficients of the IO_3^- ion in aqueous solution. L. Cavallaro (*Gazzetta*, 1942, 72, 343–350).—From the e.m.f. of $Ag|AgIO_3 \cdot KIO_3|KCl, Hg_2Cl_2|Hg$ cells in which KIO_3 varies from 0.2 to 0.02M, $\pi_{IO_3}^\circ = 0.3578$ v. (cf. Pearce *et al.*, A., 1933, 1121). Vals. of $\log f_{IO_3}$ agree with those calc. from the Debye-Huckel formula only roughly and at low concn., but agree closely with those calc. from the Bonino-Centola formula (A., 1934, 254). E. W. W.

Binary systems of cholesterol with sarcosine anhydride and antipyrine. M. Brandstatter (*Z. physikal. Chem.*, 1943, A, 192, 260–263).—Contrary to previous reports, the systems cholesterol (I)-sarcosine anhydride (II) and (I)-antipyrine do not form mixed crystals but give a mol. compound [2 mols. (I) : 1 mol. (II)] and a eutectic [102°, 47% of (I)] respectively. J. H. BA.

Miscibility and molecular compounds in the naphthalene group. A. Kofler and M. Brandstatter (*Z. physikal. Chem.*, 1943, A, 192, 229–259).—M.p.-composition curves for the ten two-component

systems which can be made from $C_{10}H_8$, α - and β - $C_{10}H_7$ -OH, and α - (I) and β - $C_{10}H_7$ -NH₂ (II) are determined. All except the (I)-(II) mixture have been examined previously, but more detailed analyses reveal differences from previous results. The system (I)-(II) shows a transition point between two forms of (II), each form giving a eutectic with (I). J. H. Ba.

Isomorphous replacement of chalcogens and ψ -chalcogens in organic compounds. H. Rheinboldt and F. Berti (*Ber.*, 1941, 74, [B], 1046—1047).—Thermal analysis by the "thaw-melt" method shows formation of mixed crystals of $COPh \cdot CH_2Ph$ (I) with $PhSBz$ [eutectic temp. 40.4° ; 53% of (I)] or $PhOBz$ [eutectic temp. 49.2° ; 74.5% of (I)]. Mixed crystals are not formed by $NHPhBz$ (II) with (I) [eutectic temp. 51.8° ; 4% of (II)], $PhOBz$ [eutectic temp. 66.3° ; 5% of (II)], or $PhSBz$ [eutectic temp. 53.7° ; 2% of (II)]. R. S. C.

Phase equilibria in hydrocarbon systems. Volumetric behaviour of n -butane. R. H. Olds, H. H. Reamer, B. H. Sage, and W. N. Lacey (*Ind. Eng. Chem.*, 1944, 36, 282—284).— P - V curves have been determined for n - C_4H_{10} at 60° intervals between 100° and 460° and at pressures $>10,000$ lb. per sq. in. The results are in accord with previous observations (A., 1939, I, 135; 1940, I, 202) and at pressures >3000 lb. per sq. in. also agree fairly well with vals. calc. from the Beattie-Bridgeman equation of state, but larger discrepancies occur at higher pressure. J. W. S.

Phase equilibria in hydrocarbon systems. Compositions of co-existing phases of the n -butane-water system in the three-phase region. H. H. Reamer, R. H. Olds, B. H. Sage, and W. N. Lacey (*Ind. Eng. Chem.*, 1944, 36, 381—383).—At temp. $>37.8^\circ$ there exist two liquid phases and one gas phase. The compositions of the gas phase and of the liquid phase of lower d were determined throughout the three-phase region. The liquid phase of lower d has a crit. temp. of 152° and a crit. pressure of 637.5 lb. per in.² J. W.

Iron-nickel-sulphur system. Introduction with new data on crystallisation of pyrrhotite and pentlandite. J. E. Hawley, G. L. Colgrove, and H. F. Zurbrigg (*Econ. Geol.*, 1943, 38, 335—388; *Nickel Bull.*, 1943, 16, 180).—Experiments showed that for low-S melts of Fe and Ni, FeS [pyrrhotite (I)] enters into a peritectic reaction with a Ni-rich liquid, forming a ternary solid solution which on final cooling is equiv. to pentlandite (II). Natural (II) appears to have a const. composition $(FeNi)_3S_8$ with Fe:Ni = 10:11. Synthetic (II) prepared from melts of varying composition ranged from 45 FeS-55 NiS to 10 FeS-90 NiS. In another series of experiments, using material of lower S content, a compound close to the composition 30 FeS-70 NiS, and approximating to the Fe:Ni ratio of $(FeS)_2Ni_3S_2$, was obtained. This compound was indistinguishable from (II). Cooling-curve data suggest that whilst the peritectic type of crystallisation may occur with low S contents, a solid-solution series between Fe sulphide and Ni sulphide may form over a still wider range. Textural relations between natural (I) and (II) are reviewed and new evidence is produced for the existence of a natural nickeliferous (I) solid solution. The mode of crystallisation of non-aq. Fe-Ni sulphide liquids is traced on the basis of studies of natural ores and experimental data. The importance of S content is emphasised. No evidence was found that such sulphide liquids are immiscible. R. B. C.

Volatility of chromium halides and equilibria in the chroming of iron. C. Wagner and V. Stein (*Z. physikal. Chem.*, 1943, A, 192, 129—156).—The v.p. of $CrCl_3$, $CrCl_2$, and $CrBr_3$ in an atm. of N_2 , and $CrCl_3$ pressures in varying HCl - H_2 mixtures, are determined at various temp. These give equilibrium consts. of the reaction $2HCl(g) + Cr(s) = H_2(g) + CrCl_2(l)$ which agree with previous determinations. These results, with the corresponding ones for the Fe system, are discussed in relation to the chroming of Fe, and vals. of the equilibrium const. for the reaction $CrCl_2(g) + Fe(s) = FeCl_2(g) + Cr(s)$ are calc. J. H. Ba.

Crystallisation volumes of the quaternary reciprocal system Na, K|F, Br, I. N. S. Dombrovskaja (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 57—60).—The constitution diagram of the Na, K|F, Br, I system, in the form of a tetrahedral prism, separates into three crystallisation vols.: (1) NaF, the largest, (2) KF, (3) continuous solid solutions of NaBr, NaI, KBr, and KI. The lowest temp. for coexistence of three solid phases is 520° , and the composition at this temp. is 4.5% NaF, 31% KBr, 31% KI, 33.5% KF. The most stable ternary diagram cross-section is NaF-KBr-KI. A. J. M.

Thermodynamics of the manganese ion. II. Thermodynamics of the manganese ion and the specific heats of ions in solution. III. Apparent volume of the manganese ion in aqueous solution. A. Kapustinski (*Acta Physicochim. U.R.S.S.*, 1942, 17, 152—166, 167—172; cf. A., 1941, I, 417).—II. The sp. heats of aq. solutions of $MnCl_2$ (0.6% to saturation) were determined at 25° , and partial molal heat capacities for the $MnCl_2$ and H_2O were calc. The apparent heat capacity is a linear function of the square root of the molal concn. Assuming that the heat capacity at infinite dilution (C_p°) of the H^+ ion is zero, C_p° vals. at 25° were calc. for Li^+ , Na^+ , K^+ , Cl^- , Br^- , I^- , SO_4^{--} , Mg^{++} , Mn^{++} , Ca^{++} , and Ba^{++} in aq. solution. C_p° can be divided into two parts; the first has a positive sign and is expended on the increase of the thermal motion of the ions in

the solution; the second has a negative sign, is larger numerically, and represents the change of ionic hydration with temp. C_p° for ions of equal valency in aq. solution is a linear function of the reciprocal of the ionic radius.

III. Determinations of d of aq. solutions of $MnCl_2$ (0.6% to saturation) were carried out at 25° . For all solutions except those of the highest concns., the formula $d^{25} = 0.9971 + 0.00786p + 1.313 \times 10^{-4}p^2$, where p is the wt.-% of $MnCl_2$, holds with an accuracy of 0.2%. From the results, the sp. vols. of the solutions and apparent molal vols. (ϕ) of the $MnCl_2$ in the solutions were calc. ϕ is a linear function of $\sqrt{(\text{molality})}$. ϕ at infinite dilution for Mn^{++} in aq. solution is -48 , indicating considerable hydration. The electrostriction curve for the system $MnCl_2$ - H_2O is similar to the curve of thermal expansion coeffs. of aq. solutions of $MnCl_2$ in its dependence on concn. J. F. H.

Heat of hydration of gaseous ions. F. H. Lee and Y. K. Tai (*J. Chinese Chem. Soc.*, 1942, 9, 41—45).—The authors' theory (A., 1943, I, 229) has been utilised to calculate the mol. heats of hydration of gaseous ions. The results for alkali and alkaline-earth metal ions are in approx. accord with the empirically deduced vals. J. W. S.

Variation of the heat of dissolution of sodium thiosulphate pentahydrate with the temperature. M. Colomina Barberá (*Anal. Fís. Quím.*, 1942, 38, 369—377).—The heat of dissolution per mol. of $Na_2S_2O_5 \cdot 5H_2O$ \propto temp. between 2.2° (-12.0) and 45.1° (-10.2 kg.-cal.), the transition temp. is at 48.0° , and at higher temp. the heat of dissolution is positive. F. R. G.

Heats of acetylation of α - and β - d -glucose from the heats of combustion of the penta-acetates. T. H. Clarke and G. Stegeman (*J. Amer. Chem. Soc.*, 1944, 66, 457—459).— ΔH of combustion at 25° and 1 atm. of α - and β - d -glucose penta-acetates have been determined calorimetrically, and are α -537.36, β -533.25 kg.-cal. per g.-mol. C_p at 25° are α -0.301, β -0.305 g.-cal. per degree per g. ΔH of formation and of the reactions d -glucose(s) + $5AcOH(l) \rightarrow d$ -glucose penta-acetate(s) + $5H_2O(l)$ and d -glucose(s) + $2.5Ac_2O(l) \rightarrow d$ -glucose penta-acetate(s) + $2.5H_2O(l)$ are: α -, -304.28 , 6.32 , and -30.88 ; β -, -302.76 , 8.92 , and -28.29 kg.-cal. per g.-mol. W. R. A.

Maxwell's demons and the second law of thermodynamics. P. Demers (*Canad. J. Res.*, 1944, 22, A, 27—51).—It cannot be regarded as possible to open a shutter between two compartments by the expenditure of an infinitesimal amount of energy, but only that of an amount $\sim kT$. The second law may be formulated "A system at a single temp. cannot produce useful work." This formulation is shown to be supported by quantum emission laws. L. J. J.

VII.—ELECTROCHEMISTRY.

Elementary mechanism of aqueous electrolysis. P. Jolibois (*Compt. rend.*, 1942, 215, 319—321).—Starting from the theory of Arrhenius, the min. potential for electrolysis and other phenomena can be explained with the help of the postulate of ions surrounded with an electrostatically charged H_2O layer. N. M. B.

Electrolytic solution pressure of copper wires under strain. L. R. Gautam and J. B. Jha (*Proc. Indian Acad. Sci.*, 1943, 18, A, 350—354).—P.d. between longitudinally strained and unstrained Cu wires, of various diam., in 0.04 and 0.004N. aq. $CuSO_4$ have been measured. The potential of the wires becomes more positive as the strain increases. It is suggested that work is necessary to detach ions from the metal surface, and that this work is greater at strained than at unstrained surfaces. W. R. A.

Correlation of solution potentials with orientations of single crystals of high-purity aluminium. C. J. Walton (*Trans. Electrochem. Soc.*, 1944, 85, Preprint 7, 71—84).—Large crystals of Al were prepared and the solution potentials of polished faces and the resistance of the faces to attack by conc. HCl were measured. The differences in solution potentials among faces of widely different orientations were <2 mv., faces with orientations approaching that of an {001} plane tending to have a lower potential than faces with orientations approaching a {111} plane. The {111} plane is more readily attacked by HCl than the {001} plane. C. R. H.

Theory of the discharge of hydrogen ions. II. Mercury. Concentrated solution of acids. S. Jofa and A. Frumkin (*Acta Physicochim. U.R.S.S.*, 1943, 18, 183—193; cf. A., 1939, I, 614).—The decrease in overvoltage (η) in conc. acid solutions is determined by the change in the boundary layer structure and the increase in $[H^+]$. The change in activity coeff. is relatively ineffective. Changes in η in HCl - KCl and HCl - $LiCl$ solutions at equal concns. are approx. equal. A linear relation is found between the adsorption potential of H^+ (ψ_1) and log (mean a val. for positive and negative ions) in the acid. The change in π is $<$ the val. calc. from the change in ψ_1 . L. J. J.

VIII.—REACTIONS.

Rupture of chains in chain reactions at the surface of solid bodies. N. N. Semenov (*Acta Physicochim. U.R.S.S.*, 1943, 18, 93—147).—The author's mathematical theory of chain reactions is applied to the

precise formulation of kinetic equations for reactions involving chain rupture at the walls in plane, cylindrical, and spherical vessels, and in cylindrical and spherical vessels of quartz or glass enclosing metallic rods or spheres. Limits of inflammation in such vessels, and in a dusty gas, and the effect of addition of inert gas, are considered. The theory of the operation of anti-detonators is quantitatively formulated. L. J. J.

Self-diffusion and chemical reaction in solids using emanation as indicator. R. Jagitsch (*Chalmers Tekn. Hogskol. Handl.*, 1942, No. 11, 47 pp.).—The use of emanation as an indicator is recommended in a rapid method of investigating self-diffusion and chemical reactions occurring between solids. The method can also be used for the investigation of the connexion between ionic migration and conductivity of electronic conductors, and for investigation of recrystallisation processes and reaction kinetics. A. J. M.

Exchange reactions between solid and liquid phases. R. Daudel (*Compt. rend.*, 1943, 217, 239—240).—In the case of a pptd. salt in a solution of a salt with the same anion, or the same cation, there is rapid exchange at first, but this soon becomes very slow. The rate of exchange during this latter stage is dependent on concn. according as there is a tendency for the ions in the solution to form complexes with the solid. Thus, with AgCl and KCl, where there is such a tendency, the rate depends considerably on [KCl], whereas with MnSO_4 and MnS the rate is almost independent of $[\text{MnSO}_4]$. A. J. M.

Chemical reactions in shock waves. J. Zeldovitch and O. Leipunski (*Acta Physicochim. U.R.S.S.*, 1943, 18, 167—171).—A gas mixture $2\text{H}_2 + \text{O}_2 + 5\text{A}$ can be ignited by firing a round-nosed Al bullet through it (impact with solid bodies being excluded) at ~ 2000 m. per sec., corresponding with a max. temp. in the gas compressed in front of the nose of the bullet of 2640°K . L. J. J.

Hydroxyl in flames. L. I. Avramenko (*Acta Physicochim. U.R.S.S.*, 1942, 17, 197—210).—The $[\text{OH}]$ in rarefied H_2 flames, with the pressure of the $\text{H}_2\text{—O}_2$ mixture ~ 40 mm., are $> 10^4$ times the equilibrium vals. Hence the chemical reaction and not equilibrium dissociation is the source of OH in the flame. The dependence of $[\text{OH}]$ on the rate of reaction confirms this result. Measurements of the distribution of OH in a rarefied cone of H_2 flame show the presence of an OH cloud around the visible cone. In non-rarefied H_2 flames the $[\text{OH}]$ becomes comparable with the equilibrium concn. J. F. H.

Thermal reactions of acetylene. I. Kinetics and mechanism of thermal polymerisation of acetylene and its reaction with nitric oxide. D. A. Frank-Kamenetzki (*Acta Physicochim. U.R.S.S.*, 1943, 18, 148—156).—The thermal polymerisation of C_2H_2 at $400\text{—}700^\circ$ and $50\text{—}780$ mm. occurs in three stages: (i) an induction period without change of pressure, (ii) a homogeneous bimol. dimerisation, (iii) a heterogeneous reaction with formation of high polymers, H_2 , and C. NO prolongs (i), and polymerisation is delayed until the NO is consumed. The temp.-dependence of (i) and (ii) corresponds with the same activation energy. The kinetics agree with a scheme involving primary combination of $2\text{C}_2\text{H}_2$ to give an unstable C_4H_4 , which can decompose into $2\text{C}_2\text{H}_2$ or two radicals, the latter at a slow rate. L. J. J.

Oxidation of beryllium. H. Terem (*Rev. Fac. Sci. Istanbul*, 1943, 8, A, 9—22).—The kinetics of the oxidation of Be have been studied to examine the validity of Valensi's law. Four samples of Be were used, containing $> 4.2\%$ Si and 0.6% Fe. For oxidation at const. temp. there is an initial induction period for all samples, that for the purest sample (0.61% Si and 0.2% Fe) being the least. In this case the amount oxidised tended to be related parabolically to the temp. and thus to react as expected from Pilling and Bedworth's generalisation (B., 1923, 359). The activation energies are different for the various samples owing to the differing degree of impurity. H_2O acts as a powerful catalyst. Oxidation in O_2 shows that nitride formation is not the cause of the inapplicability of Valensi's law as the induction period is again observed. The oxide skin formed gradually on Be at normal temp. does not greatly affect the kinetics. The mode of prep. of the powdered metal, especially the sifting, has a marked effect on the course of oxidation and rests of a few days between experiments cause an increase in the velocity owing to the absorption of H_2O by the oven. For oxidation with linearly increasing temp. the rate of oxidation increases parabolically with temp. and the general course of the reaction is independent of the rate of increase of temp. For the purest sample, oxidation is complete at 1530° . The threshold temp. of oxidation is $> 500^\circ$ and decreases with particle size. Results obtained with varying amounts of Be are compared and the optimum amount is shown to be 0.2 g. J. O'M-B.

Differential equation for the kinetics of contact unimolecular reactions investigated by the flow method. A. A. Balandin (*Acta Physicochim. U.R.S.S.*, 1942, 17, 218—223).—Theoretical. The results are applied to the dehydrogenation of alcohols and to contact isomerisation. J. F. H.

Steady-state approximation in polymerisation kinetics. W. H. Stockmayer (*J. Chem. Physics*, 1944, 12, 143—144).—The application of the Bodenstein steady-state method to the calculation of

the concn. of the free radical intermediates in vinyl polymerisations is discussed. C. R. H.

Disturbances in crystal lattices and their influence on chemical reactions and surface activity.—See A., 1944, I, 167.

History of carbonyl metals. A. Mittasch (*Kolloid-Z.*, 1943, 104, 139—141).—A review dealing chiefly with the work of the author on the kinetics of formation of $\text{Ni}(\text{CO})_4$, the prep. of Fe carbonyls and of "carbonyl" Fe from the latter by thermal decomp. The uses of "carbonyl" Fe and Ni (i.e., finely-divided Fe and Ni) are mentioned. A. J. M.

Sodium chloride as catalyst in silicate-forming reactions in the solid phase. L. M. Blumen (*J. Appl. Chem. Russ.*, 1943, 16, 81—86).—NaCl catalyses the interaction of CaO with clays, resulting in the formation of silicates and aluminates at relatively low temp. ($\sim 1000^\circ$). Trials on a large scale showed that the addition of $0.7\text{—}1\%$ of NaCl greatly improved the resistance of bricks to weather and to disintegration by H_2O . V. B.

Reactions of the type (A) solid + B (solid) \rightarrow AB (solid). IV. Review of mechanism of chemical reactions between solids. II. G. F. Huttig (*Kolloid-Z.*, 1943, 104, 189—198; cf. A., 1943, I, 22).—The changes undergone by powdered Cu and Sn in the course of gradual heating to high temp. have been investigated. Pure Cu and Sn powders, and mixtures of 3 Cu—1 Sn and 1 Cu—1 Sn, were heated in H_2 . The solubility of the heated Cu in 0.02N—HNO_3 and of Sn in 0.1N—HCl was determined. The addition of Sn reduces the reactivity of the Cu, but addition of Cu to Sn tends to increase the reactivity of the latter. Allotropic changes may explain the considerable increase in reactivity of pure Sn with acids after heating to 180° . This increase in reactivity is carried over to the Cu in mixtures of Cu and Sn, independent of composition. Pure Cu shows no increase of reactivity after having been heated to this temp. The adsorption isotherms for MeOH vapour were determined. Mixtures of Cu and Sn powders at room temp. show smaller adsorption than the individual components. This must be due to a decrease in the area of adsorbing surface. The size of the capillary pores in the mixture is between those of the components. Pure Sn adsorbs better than Cu. In the case of pure Sn there is a sudden decrease in adsorption on heating to $\sim 160^\circ$, but it rises to a max. again at 170° , after which there is a decrease to the m.p. In the mixtures, the max. was not so well defined. Vol. changes on heating were also investigated by the pycnometer method. The catalytic effect on the decomp. of H_2O_2 was studied. Catalytic activity increases if the Sn is heated to 170° , and then decreases, at first slowly, then rapidly. The catalytic activity in the case of (3 Cu—1 Sn) was the same as, or with (1 Cu—1 Sn) $>$, that of the components. The results are discussed on the supposition of the occurrence of a diffusion process, and the existence of an adsorption layer. The effects taking place when the substances are heated over the range $150\text{—}200^\circ$ are specially considered. A. J. M.

Kinetic study on the dehydrogenation of cyclohexane. A. A. Balandin and F. L. Kostin (*Acta Physicochim. U.R.S.S.*, 1942, 17, 211—217).—The catalytic dehydrogenation of cyclohexane was investigated at $380\text{—}530^\circ$ with Cu on Cr_2O_3 (I), Cu on Cr_2O_3 with BaO (II), and Cr_2O_3 from $\text{Cr}_2(\text{CrO}_2)_3$ (III) as catalysts. C_6H_6 is the main product, the yields at 530° being 100% with (I), 13% with (II), and 51% with (III). Contrary to usual results, catalyst (III) did not lose its activity after 80 hr. in use. With increasing temp. the yield of unsaturated hydrocarbons obtained with (III) decreased. Determination of the activation energy and the pre-exponential factor for the reaction show that the sextet mechanism proposed previously (A., 1937, I, 90) is operative for reaction on catalyst (I); in the other cases the duplet mechanism occurs. J. F. H.

Polymerisation of isobutene on hydrated silicate catalysts. IH. B. A. Kazanski and M. I. Rozengart (*J. Gen. Chem. Russ.*, 1943, 13, 304—308).—Products, similar in composition and yield, are obtained when $\text{iso-C}_4\text{H}_8$ (I) is polymerised in the presence of Gayer (hydrated $\text{Al}_2\text{O}_3\text{—SiO}_2$) catalyst or of "solid phosphoric acid" ($\text{H}_3\text{P}_2\text{O}_7$ on kieselguhr); a similarity in their mode of action is indicated. Catalysts prepared by Gayer's method (B., 1933, 997), in which Al is replaced by Zn or Ti, are incapable of polymerising (I). A similar Th catalyst was active but rapidly became poisoned by deposition of non-volatile products; this catalyst showed a very mild action, since the liquid product contained almost 50% of diisobutene and practically no isomeric dimerides. It is suggested that these catalysts owe their activity to the acidic properties of the hydrated metallic silicates dispersed over the surface; the neutral silicates (of Zn and Ti) are inactive. R. C. P.

Catalytic behaviour of thermally-pretreated copper powder with respect to the decomposition of formic acid vapour. K. Sedlátschek (*Kolloid-Z.*, 1943, 104, 203—208).—Cu powder was heated to various temp. in HCO_2H or H_2 and the activity as regards catalytic decomp. of HCO_2H vapour was determined. The activity was considerably affected by this pretreatment, the activation energy showing two max. ($250\text{—}280^\circ$ and 540°). These are explained by consideration of the processes taking place during the preheating, some affecting the surface, others the lattice. Preheating in HCO_2H vapour brings

the max. closer together, and makes it more difficult to distinguish between surface and lattice processes. The decomp. of HCO_2H vapour by the same catalyst is reproducible, but it is difficult to prepare Cu catalysts of the same activity. Reproducibility of activation energy can be more easily attained than activity and no. of active centres. The activation energy of Cu powders depends on how long they are kept between periods of use, and in what atm. A. J. M.

Catalytic vapour-phase oxidation of fatty oils.—See B., 1944, II, 172.

Electrolysis of fused sodium sulphate. I. H. vom Hove and F. Müller (*Z. anorg. Chem.*, 1943, 250, 377—388).—Metals, C, and electrically-conducting metallic sulphides are attacked by fused Na_2SO_4 , but Fe_3O_4 is unchanged. In the electrolysis of fused Na_2SO_4 between Fe_3O_4 electrodes, SO_2 or SO_3 and O_2 are evolved at the anode and Na_2O is formed at the cathode. At the same time the cathode is converted into NaFeO_2 , and Na_2SO_3 , Na_2S , and FeS are formed by cathodic reduction. F. J. G.

Chemiluminescence of lucigenin. B. J. Sveschnikov and P. P. Dikun (*Acta Physicochim. U.R.S.S.*, 1942, 17, 173—184).—The kinetics of chemiluminescence of lucigenin (I) in aq. H_2O_2 -NaOH solution were studied at 18° and 50°. The behaviour is similar to that observed with 3-acetamidophthalhydrazide (II) (A., 1938, I, 600), the main difference being that the curve connecting intensity of luminescence with time for (I) shows no max. This is in part contradictory to Drew's hypothesis (A., 1939, I, 125), but it appears that the first stage of the luminescence process is the same for (I) and (II), viz., the formation of a peroxide. J. F. H.

Mercury-photosensitised polymerisation of acetylene. D. J. Le Roy and E. W. R. Steacie (*J. Chem. Physics*, 1944, 12, 117—124).—The rate of the Hg^3P_1 -photosensitised polymerisation of C_2H_2 at 25° increases rapidly with pressure up to ~5 mm., but at higher pressures the increase is less marked. The rate increases with temp. up to ~250° and then decreases, the temp. coeff. being small. The quantum yield is 4.5 ± 1.2 at 25° and 40 mm. Polymerisation is inhibited by NO, indicating that free radicals rather than excited mols. are involved, and a probable mechanism for such a reaction is suggested, the primary step being $\text{Hg}^3\text{P}_1 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H} + \text{Hg}(\text{S})_0$ $\text{C}_2\text{H} + \text{HgH}$ or $\rightarrow \text{HgC}_2\text{H} + \text{H}$. Inhibition by NO also occurs when the reaction is photosensitised by Cd^8P_1 or Cd^1P_1 . C. R. H.

Action of X-rays on hydrogen sulphide. J. Loiseleur (*Compt. rend.*, 1942, 215, 536—537).—Under the action of Mo K_α radiation, an aq. solution of H_2S undergoes "electrolysis" with liberation of S. Measurements show that the amount of S increases with the concn. of the solution, and, for very small concns., the S is suspended in colloidal form, but appears as a rapidly settling ppt. at higher concns. N. M. B.

Spectral study of a luminescent reaction.—See A., 1944, I, 116.

Piccardi phenomenon. Measurement of activation and character of crystalline deposits from activated [natural] water. A. Manfredi (*Gazzetta*, 1942, 72, 529—537).—The temp. at which microcrystals of CaCO_3 appear on the surface of hard natural H_2O is reduced by "T" activation (cf. Piccardi, A., 1940, I, 112), and increased by "R" activation by a high-frequency discharge between a stainless steel electrode and a Ciccotti element (a Ne tube with single central electrode; cf. C., 1944, Part 3). Increase in temp. is const. for const. activation, and increases smoothly with time of activation. The greater is the increase in temp., the smaller are the microcrystals formed. E. W. W.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Cyclotron targets. Preparation and radiochemical separation. II. Krypton. S. C. Brown, J. W. Irvine, jun., and M. S. Livingston (*J. Chem. Physics*, 1944, 12, 132—134).—If NaBr is bombarded with neutrons and the crystals, which contain radioactive Na, Br, and Kr, are melted in a monel metal tube, the released gas contains radioactive Kr free from measurable amounts of radioactive Br. Another method is to bombard fused and powdered NaBr and to dissolve the powder in 0.01M-NaOH under reduced pressure. The radioactive Kr is removed by sweeping CO_2 through the solution. C. R. H.

Preparation of sodium nitrite. W. T. Cooke (*J. Proc. Austral. Chem. Inst.*, 1944, 11, 49—51).—A charge of NaNO_3 is melted with Pb in an Fe ladle at 400—450°. The reaction $\text{Pb} + \text{NaNO}_3 = \text{PbO} + \text{NaNO}_2$ proceeds rapidly on the surface but lengthy heating and stirring are necessary to produce a good yield. After cooling, the melt is treated with H_2O , any sol. Pb removed by a current of CO_2 , and nitrous fumes are aspirated through the liquor to neutralise excess of alkali. Fractional crystallisation yields first crops containing 85—90% of NaNO_2 . Further low-grade crops are best fused again with Pb. J. C. C.

Preparation of cupric sulphate by aerial oxidation. K. K. Jau and C. T. Hsu (*J. Chinese Chem. Soc.*, 1943, 10, 40—47).—The rate of dissolution of Cu in H_2SO_4 (0.5—6N.) in presence of air has been

studied by repeatedly pouring the acid over scrap Cu and also by intermittent immersion of Cu plates in the acid. The rate of dissolution during intermittent immersion in H_2SO_4 saturated with CuSO_4 has also been studied. From the results it is inferred that 2N- H_2SO_4 causes most rapid dissolution and also dissolves the largest total amount of Cu. J. W. S.

Ammine of basic copper chromate. W. H. Hartford (*J. Amer. Chem. Soc.*, 1944, 66, 312).—Basic Cu carbonate (14.3) and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (4.4 g.) in H_2O (40 ml.) with conc. aq. NH_3 (50 ml.) at room temp. (not colder) give the compound, $2\text{CuO} \cdot 4\text{NH}_3 \cdot \text{CrO}_3 \cdot \text{H}_2\text{O}$.

Complex compounds of cupric azide. VI. Azidocuprates of the elements of the first and second groups of the periodic system. M. Straumanis and A. Cirulis (*Z. anorg. Chem.*, 1943, 252, 121—126).—The following azidocuprates are described: $\text{K}[\text{Cu}(\text{N}_3)_2] \cdot \text{H}_2\text{O}$; $\text{K}[\text{Cu}(\text{N}_3)_2]$; $\text{Rb}[\text{Cu}(\text{N}_3)_2]$ (I); $\text{Cs}[\text{Cu}(\text{N}_3)_2]$ (II); $\text{Sr}[\text{Cu}(\text{N}_3)_2] \cdot 3\text{H}_2\text{O}$ (III). (I) explodes at 230—233°, (II) at 210°; both are sensitive to shock. (III) explodes on dehydration. F. J. G.

Preparation of calcium and sodium formates. N. N. Zabolotskaja, E. I. Lukianova, and D. N. Schoichet (*J. Appl. Chem. Russ.*, 1943, 16, 118—128).—The production of $(\text{HCO}_2)_2\text{Ca}$ by the direct action of CO or of producer gas on $\text{Ca}(\text{OH})_2$ is catalysed by alkali metal salts. Optimum conditions are a temp. of 180—200° and CO pressure of 20—25 atm. The presence of H_2O (0.5 atm.) is desirable. HCO_2Na can be simultaneously obtained by the action of CO on equimol. mixtures of $\text{Ca}(\text{OH})_2$ with Na_2CO_3 or Na_2SO_4 . The max. yield of HCO_2Na (89.7%) was obtained with the former at 6 atm. CO at 200° for 7½ hr. With 8 atm. producer gas at 200° for 24 hr. the conversion into HCO_2Na was 88.7%. V. B.

Gallium trimethyl. E. Wiberg, T. Johannsen, and O. Stecher (*Z. anorg. Chem.*, 1943, 251, 114—124).— GaMe_3 is formed quantitatively from Ga and HgMe_2 at 130°. It has m.p. -15.8° and v.p. at 0° = 64.5 mm. With H_2 in the glow discharge it affords $\text{Ga}_2\text{H}_6\text{Me}_2$, with I at 60° GaI_3 and MeI, and with HI, GaI_3 and CH_4 . With NMe_3 it forms $\text{GaMe}_3 \cdot \text{NMe}_3$, m.p. 96.2°, and with NEt_3 , $\text{GaMe}_3 \cdot \text{NEt}_3$, m.p. 96.0°. Data on v.p. and heats of sublimation and vaporisation for these are given. F. J. G.

Phenol-p-sulphonates of lanthanum [and other metals]. G. Manelli (*Gazzetta*, 1943, 73, 105—108).—($p\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3$)₂La and $\text{M}_2(\text{SO}_4)_3$ give La, Pr, Nd, and Sm phenol-p-sulphonates, ($p\text{-OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3$)₂M, $6\text{H}_2\text{O}$. These are too sol. in H_2O to be useful for fractionation. E. W. W.

Diamond problem. P. L. Günther, P. Geselle, and W. Rebentisch (*Z. anorg. Chem.*, 1943, 250, 357—372).—Attempts to synthesise diamond (I) by modifications of Moissan's method, and by subjecting C for a short time to pressures of 120,000 atm. at 3000—3200°, all failed. (I) is unchanged in contact with Fe melts rich in C at >2000°, but rapidly changes to graphite at higher temp. F. J. G.

Effect of transformation temperature of supercooled austenite on composition of separated carbides. N. N. Sirota (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 111—114).—Mathematical. The composition of the carbides separating from a supercooled austenitic steel approximates the more nearly to pure Fe_3C the smaller is the particle size, i.e., the lower is the transformation temp. M. H. M. A.

Germanium. XIX. Polymorphism of germanium dioxide. R. Schwarz and E. Haschke (*Z. anorg. Chem.*, 1943, 252, 170—172).—The transformation of pure specimens of the sol. hexagonal modification (I) of GeO_2 into the insol. modification (of rutile type) is often strongly inhibited, but occurs easily at <380° in presence of small amounts of NH_4F , provided that (I) is initially in thin flakes as obtained by slow evaporation. F. J. G.

Preparation and stability relations of black phosphorus. P. L. Günther, P. Geselle, and W. Rebentisch (*Z. anorg. Chem.*, 1943, 250, 373—376).—Ordinary white P (I) is converted into Bridgman's black P (II) at room temp. by a pressure of 100,000 atm. If not completely freed from traces of (I), (II) changes spontaneously into (I) under ordinary conditions. F. J. G.

Chemistry in liquid sulphur dioxide. XII. Preparation of some anhydrous tetramethylammonium compounds and their behaviour in liquid sulphur dioxide. G. Jander and H. Hecht (*Z. anorg. Chem.*, 1943, 250, 304—311).—The following NMe_4 compounds are described: $(\text{NMe}_4)_2\text{S}_2\text{O}_8$; $(\text{NMe}_4)_2\text{S}_2\text{O}_7$; $\text{NMe}_4\text{SbCl}_4$. Their behaviour in liquid SO_2 is described. F. J. G.

Chemistry in liquid sulphur dioxide. XI. Amphoteric behaviour of some sulphites or oxides in liquid sulphur dioxide. G. Jander and H. Hecht (*Z. anorg. Chem.*, 1943, 250, 287—303).—When $(\text{NMe}_4)_2\text{SO}_3$, which is the analogue of a strong base in the SO_2 system, is added to solutions of SnCl_4 , SiCl_4 , SbCl_3 , SbCl_5 , and GaCl_3 in liquid SO_2 , ppts. are obtained which redissolve in excess. Conductometric titration curves are in accord with reactions analogous to the pptn. and redissolution of an amphoteric hydroxide in the H_2O system. Sn dissolves in a solution of $(\text{NMe}_4)_2\text{SO}_3$ in liquid SO_2 , and the reaction products contain Sn^{IV} and $\text{S}_2\text{O}_8^{2-}$. This reaction is interpreted on the same analogy. F. J. G.

Salts of phenolsulphonic acids. G. Manelli (*Gazzetta*, 1943, 73, 109—113).—The solution derived from aq. $(p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3)_2\text{Ba}$ (I) and CuSO_4 when treated with an aq. $\text{Ca}(\text{OH})_2$ gives the *basic salt* $\text{C}_6\text{H}_4\text{O}_{10}\text{SCu}_4$. The solution from (I) and ZnSO_4 gives only $\text{Zn}(\text{OH})_2$. E. W. W.

Reactions in liquid ammonia. I. Ammonolysis of hexavalent chromium derivatives. H. H. Sisler (*Trans. Kansas Acad. Sci.*, 1943, 46, 136—141).— KCrO_4Cl (I) is prepared by adding CrO_3Cl_2 dropwise to aq. K_2CrO_4 at 100° , cooling, and separating (I). CrO_3 or (I) and excess of liquid NH_3 (-80° to 0°) give Cr_2O_3 ($\sim 25\%$ of the total Cr) and an insol. yellow product (II); at 0° in a sealed tube the reaction mixture often inflames. It is suggested that (II) is an ammonio-chromate. M. H. M. A.

Tungsten oxides. O. Glemser and H. Sauer (*Z. anorg. Chem.*, 1943, 252, 144—159).—W oxide preps. were synthesised from W and WO_3 , and their X-ray diagrams, ρ , and conductivity determined. The following phases exist: α , WO_3 to $\text{WO}_{2.95}$, in which the least deficiency of O below WO_3 produces a blue colour; β , $\text{WO}_{2.92}$ to $\text{WO}_{2.88}$; γ , $\text{WO}_{2.76}$ to $\text{WO}_{2.65}$, which gives an X-ray diagram identical with that of the oxide W_5O_{11} described by Ebert and Flasch (A., 1934, 378) although their interpretation is not confirmed; δ , $\text{WO}_{2.05}$ to WO_2 . There is no oxide lower than WO_2 . Products obtained by reduction of WO_3 with H_2 - H_2O mixtures were identical with these phases, but reduction of H_2WO_4 afforded instead of β two new phases which contain H. Both of these on further reduction afford γ . One of them has the ReO_3 structure with $a = 3.746 \text{ \AA}$. It is the H-analogue of the W bronzes, and may be formulated $\text{WO}_{3-n}\text{H}_2$ where $n < 1$, and in which the H atoms are irregularly placed in the lattice. The other new phase is closely related to this, and so are the so-called hydroxides of Ebert and Flasch (A., 1936, 174). F. J. G.

Composition of tungsten-blue. O. Glemser and H. Sauer (*Z. anorg. Chem.*, 1943, 252, 160—163).—The composition of W-blue depends on the conditions of its formation. Specimens which are oxidisable in air contain the α phase of the W-O system (cf. preceding abstract), with an O content somewhat $<$ that of WO_3 , whereas those stable in air contain $\text{WO}_{3-n}\text{H}_2$. F. J. G.

Partial separation of uranium light isotope by thermomdiffusion. A. E. Brodski (*Acta Physicochim. U.R.S.S.*, 1942, 17, 224—227).—Calculations are made of the necessary equipment and efficiency for the separation of ^{235}U by thermal diffusion using UF_6 . The energy expended in separation is 40—80% of that yielded by fission of the ^{235}U nuclei. J. F. H.

Enrichment of ^{37}Cl in carbon tetrachloride by thermal diffusion. A. Fournier (*Compt. rend.*, 1942, 215, 529—530).—Experiments by the Clusius-Dickel method are reported. The enriched CCl_4 is subjected to the transformation steps $\text{CCl}_4 \rightarrow \text{CHCl}_3 + \text{ZnCl}_2 \rightarrow \text{AgCl}$, and the enrichment is detected by measurements of ρ and n . N. M. B.

Decomposition of hypochlorites in solution. P. Pierron (*Compt. rend.*, 1942, 215, 354—355).—Investigations on the salts of Na, K, and Li, under similar sets of conditions of temp., concn., alkalinity, and acidity, indicate the transitional formation of peroxides which effect decomp. of one part of the hypochlorite into chloride and O_2 and oxidation of the other part to chlorate. N. M. B.

Cyanic acid. V. Carbamate-cobaltic complexes. M. Linhard and H. Flygare (*Z. anorg. Chem.*, 1943, 251, 25—44).—Attempts to prepare cyanato-complexes by the action of KOCN or AgOCN on aquo-cobaltamine salts results in the formation of carbamate-complexes. The reaction is rapid and notably exothermic ($q \sim 15 \text{ kg.-cal. per g.-mol.}$) and involves direct addition of the OCN^- ion to the complex-bound H_2O mol. The following compounds are described: $\text{X}(\text{NO}_2)_3$ (I); $\text{XSO}_4\cdot\text{H}_2\text{O}$ (II); $\text{X}(\text{HSO}_4)_2$; XBr_2 (III); XI_2 (IV); XS_2O_8 (V); $\text{XCrO}_4\cdot x\text{H}_2\text{O}$ [$\text{X} = \text{Co}(\text{NH}_3)_4\text{CO}_2\cdot\text{NH}_2$]; $\text{Y}(\text{NO}_2)_3$; YS_2O_8 [$\text{Y} = \text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{CO}_2\cdot\text{NH}_2$]. Solubilities are recorded as follows: (I), 0.0778; (II), 0.220; (III), 0.629; (IV), 0.188; (V), 0.0005 g.-mol. per l. at 20° . F. J. G.

Composition and mechanism of formation of nickel hydrides. I. Composition. A. A. Balandin, B. V. Jerofeev, K. A. Pecher-skaja, and M. S. Stachanova (*Acta Physicochim. U.R.S.S.*, 1943, 18, 157—166).—Ni hydride is formed in the reduction of NiCl_2 with organo-Mg halide solutions in an atm. of H_2 , and has the composition NiH_4 , whilst NiH_2 is absent in these conditions. NiH_4 has been isolated and analysed by decomp. at 100° . Excess over the theoretical amount of H_2 is absorbed during the prep. of NiH_4 , owing to catalysis of hydrogenation of the C_6H_6 nucleus of the MgPhCl used. NiH_4 is formed by the partial decomp. of NiH_4 . L. J. J.

Metallic carbonyls. XLV. Rhodium in the system of the metallic carbonyls. W. Hieber and H. Lagally (*Z. anorg. Chem.*, 1943, 251, 96—113).—The compound prepared by Manchot and König (A., 1925, ii, 1193) by the action of CO on hydrated RhCl_3 at $>100^\circ$, and formulated $\text{Rh}_2\text{OCl}_3\cdot 3\text{CO}$, is *Rh dicarbonyl monochloride*, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, m.p. 123° . The corresponding bromide, $[\text{Rh}(\text{CO})_2\text{Br}]_2$, m.p. 118° , is

formed under analogous conditions, and these and the *iodide*, $[\text{Rh}(\text{CO})_2\text{I}]_2$, m.p. 114° , may be obtained by high-pressure synthesis from the anhyd. halides and CO. High-pressure synthesis with CO and either metallic Rh or RhCl_3 in presence of Cu or Ag under various conditions affords the following *Rh carbonyls*: $[\text{Rh}(\text{CO})_4]_2$, m.p. 76° ; $[\text{Rh}(\text{CO})_3]_2$, decomp. 150° ; and $[\text{Rh}_4(\text{CO})]$ decomp. 220° , and *Rh carbonyl hydride*, $\text{Rh}(\text{CO})_4\text{H}$, m.p. -10° to -12° . F. J. G.

Hydroxylamine and hydrazine complex compounds of platinum and palladium. I. Hydroxylamine compounds of platinum. V. I. Goremikin and K. A. Gladischevskaja (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 108—116).— Pt^{II} in *cis*-platotetrammines can be oxidised by NH_2OH to Pt^{IV} with formation of "inorganic quinhydrones." *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{NH}_2\text{OH})_2]\text{Cl}_2$ with 48% HBr at 100° yields the compound $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})\text{Br}_2][\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})\text{Br}_2]$ (I), brown crystals stable at 110° which are decomposed by COMe_2 to $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})\text{Br}_2]$ (II), isolated after being transformed into $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})(\text{CS}(\text{NH}_2)_2)]\text{Br}_2$, and the compound $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})\text{Br}_4]$ (III), orange crystals. (I) is obtained also by moistening a powdered mixture of (II) and (III) with dil. HBr . In a small yield are obtained the compounds: *trans-trans*- $[\text{Pt}(\text{NH}_2\text{OH})_2\text{Br}_2][\text{Pt}(\text{NH}_2\text{OH})_2\text{Br}_4]$, brown crystals, by heating $[\text{Pt}(\text{NH}_2\text{OH})_2]\text{Cl}_2$ or $[\text{Pt}(\text{NH}_2\text{OH})_2](\text{OH})_2$ with 30% HBr , and *trans-trans*- $[\text{Pt}(\text{NH}_2\text{OH})(\text{C}_6\text{H}_5\text{N})\text{Br}_2][\text{Pt}(\text{NH}_2\text{OH})(\text{C}_6\text{H}_5\text{N})\text{Br}_4]$, brown crystals, from *cis*- $[\text{Pt}(\text{NH}_2\text{OH})(\text{C}_6\text{H}_5\text{N})]\text{Cl}_2$ and 20—30% HBr . J. J. B.

XI.—GEOCHEMISTRY.

Chemistry of sea-water: elements present in traces. H. Wattenberg (*Z. anorg. Chem.*, 1943, 251, 86—91; cf. A., 1938, I, 280). F. J. G.

Chemistry of sea-water: dissolved gases. H. Wattenberg (*Z. anorg. Chem.*, 1943, 251, 71—85).—A review. Methods of analysis and equilibrium relationships and distribution of A , N_2 , O_2 , and CO_2 (CO_2 , HCO_3^-) various depths are discussed (see also C., 1944, Part 3). F. J. G.

Carboniferous brines of the Polasna-Krasnokamsk anticline. A. M. Kuznetsov and S. N. Novikov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 61—64).—Brines containing H_2S were found during oil-drilling in the Middle and Lower Carboniferous rocks of the Kama region. They are saturated with CaSO_4 . The pH does not vary greatly (4.11—4.63); $[\text{Ca}]/[\text{Mg}] = 1.86\text{—}2.85$; $[\text{NH}_4]/[\text{Br} + \text{I}] = 0.87\text{—}1.39$. $[\text{H}_2\text{S}]$ in H_2O from the top portion of the Carboniferous rocks is 0.45 g. per 1000 g. In sub-oil H_2O it is 0.16 g. per 1000 g. In the edge H_2O , $[\text{H}_2\text{S}]$ is very small, and no H_2S was found in the H_2O of the coal-bearing series, or at the bottom of the Carboniferous. This may be due to the physiological equilibrium of the solution being disturbed by the accumulation of Ca^{++} and Mg^{++} . A. J. M.

Composition of colloid dispersion minerals and the metathetic capacity of glauconites from Saratov [Russia]. I. N. Antipov-Karataev and I. D. Sedletzki (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 115—117).—"Glauconites" from Lyssaya Gora (Saratov) contain glauconite ~ 50 , montmorillonite ~ 40 , and sericite $\sim 10\%$. The X-ray picture remains unchanged on substitution of H, Li, Mg, Na, or Ba for the replaceable cations. The metathetic ability (B.E.V.) for M-BaCl_2 at pH 9 is 31.1 m-equiv. per 100 g. M. H. M. A.

Action of hydrofluoric acid on muscovite. R. Delavault (*Compt. rend.*, 1942, 215, 582—584).—Two different forms of corrosion due to the boiling acid are discussed; one is related to the crystal lattice structure, and the other to physical irregularities or the presence of impurities. N. M. B.

X-Ray scattering from chrysotiles.—See A., 1944, I, 119.

The Panjal traps: acid and basic volcanic rocks. P. N. Ganju (*Proc. Indian Acad. Sci.*, 1943, 18, B, 125—131).—Chemical analyses are recorded and discussed. L. S. T.

Sulphur in the Buguruslan [Russia] oil region. G. I. Theodorovitch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 39, 118—120).—The Buguruslan oilfield is covered in the west by anhydrite (20—30 m.), which splits towards the east into two seams separated by halite. No free S occurs in or above the oilfield itself, but, except on the eastern side, free S occurs around the edges of the field in the zone of oil- H_2O contact. Formation of S probably proceeds by $\text{SO}_4^{--} \rightarrow \text{H}_2\text{S}$ (bacterial?), followed by oxidation of H_2S by O_2 dissolved in mobile stratum H_2O , which originates to the N.N.W. of the oilfield. In the eastern boundary the stratum H_2O is not mobile and thus does not carry O_2 ; H_2S formed from SO_4^{--} appears in this region as FeS_2 . It is concluded that inclusions of free S under anhydrite are evidence of the near presence of oil-bearing strata. M. H. M. A.

Statistical study of bioclimatic influence on the chemico-mineralogical characteristics of the soil of the Ivory Coast (silica-alumina relation). L. Galangeaud (*Compt. rend.*, 1942, 215, 360—362).—Curves are given and discussed. N. M. B.

A I—General, Physical, and Inorganic Chemistry.

SEPTEMBER, 1944.

I.—SUB-ATOMICS.

Direct derivation of Balmer spectra. D. D. Kosambi (*Current Sci.*, 1944, 13, 71—72).—Mathematical. N. M. B.

Energy transport by radiation in resonance lines of gases. R. Mannkopff (*Z. Physik*, 1943, 120, 301—317).—The transference of energy between different portions of a gas at different temp. by radiation and absorption in resonance $\lambda\lambda$ is calc. for limited and unlimited vol. The result is applied to energy transference in the electric arc. L. J. J.

Structure of the second spark spectrum of bromine, Br III. K. R. Rao (*Current Sci.*, 1944, 13, 72).—Many intercombination lines in the optical and vac.-grating region have been identified. The interval $4p^4S_{3/2}—4p^2D_{3/2}$ is 16042 cm.^{-1} and $4p^2D_{5/2}—4p^2P_{1/2}$ is 10613 cm.^{-1} . N. M. B.

Quadrupole moment of the atomic nucleus ^{181}Ta . T. Schmidt (*Z. Physik*, 1943, 121, 63—72).—The hyperfine structure of the terms $5d^36s^2$, $4f_{3/2, 5/2, 7/2}$ and $4p_{3/2}$ of the Ta I spectrum is studied by means of a Fabry-Perot interferometer, and the coupling consts. are found. The mathematical method for calculating the quadrupole moment (involving the use of matrices) is presented and the val. of the moment is found to be $+6 \times 10^{-24}$. L. S. G.

K Absorption spectra of elements with atomic numbers 71 (Lu), 70 (Yb), 68 (Er), 66 (Dy), 64 (Gd), and 63 (Eu). (Mlie.) I. Manescu (*Compt. rend.*, 1943, 217, 69—71).—The K absorption spectra of the above elements have been investigated, and the principal discontinuities determined. A. J. M.

Auger transitions and widths of X-ray energy levels. J. N. Cooper (*Physical Rev.*, 1944, [ii], 65, 155—161).—Since rapid variations of line width with at. no. are to be expected when sudden changes in Auger transition probabilities occur, at. no. ranges where large variations might be expected were studied. Part of the width variation of $L\beta_3$ for elements 73—92 is attributed to the Auger transitions $M_{III} \rightarrow M_{IV}N_{IV, V}$. The transitions $N_{II} \rightarrow N_{III}O_{II, III}$, $N_{II} \rightarrow N_{IV, V}N_{IV, V}$, and $N_{III} \rightarrow N_{IV, V}N_{IV, V}$ explain an intensity anomaly of $M\zeta$ for elements 38—58. Other irregularities are correlated. Evidence supports the theory that Auger transitions are primarily responsible for anomalous changes in line width. N. M. B.

Ionisation cross-section of the silver L_{III} state. J. J. G. McCue (*Physical Rev.*, 1944, [ii], 65, 168—175).—Measurements were obtained by observing the intensity of the $L\alpha$ doublet radiation from a thin Ag target bombarded by cathode rays of energy >9 times the excitation energy of the L_{III} state, and correcting for effects of diffusion, rediffusion, and retardation of the cathode rays. Cross-sections agree fairly well with calculations based on the Born approximation, but are outside estimated experimental error. N. M. B.

L X-Ray spectrum of radium-D. M. Valadares (*Portugaliae Physica*, 1944, 1, 73—75).—Apparatus for the investigation of the X-ray spectrum of Ra-D is described. 0.04 g. of Ra is used. A. J. M.

Photo-electric primary current in crystals of alkali halides. F. Domancik (*Ann. Physik*, 1943, [v], 43, 187—192).—The photo-electric primary current in KCl and KBr crystals, measured by the product of quantum yield and electron path in unit field, shows approx. the same dependence on temp. and concn. of F-centres when F-centres are taken as electron sources as when F-centres act as such sources. A. J. M.

Secondary emission of films of pure metals in ordered and disordered states and their transparency to electrons. R. Suhrmann and W. Kundt (*Z. Physik*, 1943, 120, 363—382).—The yield of secondary electrons at 83°K . from thin films of Cu, Ag, Au, and Be condensed on glass has been studied as a function of the primary electron acceleration voltage. The films pass from a disordered to an ordered at. configuration on heating momentarily to room temp. In the ordered state the yield of secondary electrons is smaller, particularly from fast primary electrons. The effect is correlated with an increase in the electron-transparency of the films, particularly for fast electrons, on passing to the ordered state, but this effect is insufficient to account for the difference in yield, which is partly due to a decrease in the no. of secondarily-emitting centres.

Conversion factors from international to absolute electrical units. U. Stille (*Z. Physik*, 1943, 121, 34—53).—The vals. of the conversion factors are studied as a preliminary to a discussion of the vals. of the at. consts. (the latter being derived from new and precise measurements of e , e/m_0 , and h/e ; see following abstract). The best vals. at present are found to be 1 international ohm = 1.00049 ± 0.00002 abs. ohms and 1 international amp. = 0.9999 ± 0.0001 abs. amp. L. S. G.

The atomic constants e , e/m_0 , and h . U. Stille (*Z. Physik*, 1943, 121, 133—200).—The experimental data available for the determination of at. consts. are collected and discussed. The following vals. are taken as established for velocity of light in vac. (c_0), induction const. (μ_0), influence const. (e_0), sp. mol. no. (N_L) and sp. ionic charge (F): $c_0 = 2.99777 \pm 0.00020 \times 10^8\text{ m. per sec.}$, $\mu_0 = 1.25602 \pm 0.00002 \times 10^{-6}\text{ v. sec./amp. m.}$, $e_0 = 8.8594 \pm 0.0014 \times 10^{-12}\text{ amp. sec./v. m.}$, $N_L = 6.0243 \pm 0.0048 \times 10^{23}\text{ k.-mol.}^{-1}$, and $F = 9.6520 \pm 0.0006 \times 10^7\text{ A. sec./k.-equiv.}$; the last two vals. refer to the physical at. wt. scale. The vals. found for the electronic charge (e), sp. electronic charge (e/m_0), and the Planck const. (h) are: $e = 1.6022 \pm 0.0014 \times 10^{-19}\text{ coulomb}$, $e/m_0 = 1.7593 \pm 0.002 \times 10^{11}\text{ coulomb per kg.}$, and $h = 6.619 \pm 0.010 \times 10^{-34}\text{ w. sec.}^2$. Vals. for the Rydberg const. (R_∞) and the Sommerfeld fine structure const. (a), calc. from the best available data, are: $R_\infty = 10,973,730.4 \pm 7.8\text{ m.}^{-1}$ and $a = (136.95 \pm 0.13)^{-1}$. There is no ground for assuming any deviation from the fundamental theoretical laws on the basis of existing experimental data. L. J. J.

Atomic-reaction apparatus for potential differences up to 1 million volts. M. von Ardenne (*Z. Physik*, 1943, 121, 236—267).—The apparatus is described in detail. A van de Graaff band-generator working at atm. pressure and a multi-stage discharge tube are employed. The discharge tube operates with electrons, protons, or deuterons at will, with a beam strength of $\sim 35\text{ }\mu\text{A}$, and gives a Ra-Be equiv. for the Li + D reaction of $\sim 65\text{ g. of Ra}$. The energy consumption is minimised by the use of beam focussing by means of a directing electrode. The pumping speed required is 30 l. per sec. and 20% of the generator current is available in the beam. L. J. J.

New type of electron. A. Proca (*Portugaliae Physica*, 1944, 1, 69—65).—Relativity considerations suggest the existence of a particle differing from the Dirac electron. Though it has the same mass, charge, and spin as the Dirac electron, its energy varies. A. J. M.

Mobilities of electrons in helium. F. L. Jones (*Proc. Physical Soc.*, 1944, 56, 239—248).—Mobilities are calc. over the range $Z/p = 0.5—3.0\text{ v. cm. per mm. Hg}$ on the basis of an energy distribution formula previously found applicable to the electron energy range for excitation and ionisation in the uniform positive column in He (cf. A., 1936, 771). When the observed variation of at. cross-section with electron velocity is taken into account, the calc. mobilities show good agreement with accepted measured vals. N. M. B.

Mobility of free electrons in argon. P. Herreng (*Compt. rend.*, 1943, 217, 75—77).—A method of determining the velocity of free electrons in a gas under the action of a uniform electric field consists in ionising a thin section of the gas by very short periodic bursts of X-rays, and studying the variation of current in the chamber circuit by means of an oscillograph. Results agree well with those of other workers. The mobility is a function of the ratio E/p (E —intensity of field, p —pressure of gas). The mobility is plotted against E/p and the results are discussed. A. J. M.

Scattering and polarisation of fast electrons by heavy elements. C. B. O. Mohr (*Proc. Roy. Soc.*, 1943, A, 182, 189—199).—The results of a previous paper (A., 1941, I, 191) are applied to the calculation of the scattering and polarisation of electrons with 5.4 to 1060 ke.v. energy by the at. field of Au. Even at the highest energies the angular distribution of the scattering does not exhibit a monotonic fall with increasing angle. The asymmetry in double scattering reaches a max. val. which is large at angles $>90^\circ$. In connexion with the discrepancies between different observers for the scattering and polarisation at 90° , it is shown that the addition of a long-range repulsive field to the field of the atom reduces the asymmetry in double scattering by a large factor. G. D. P.

Influence of adsorbed oxygen on the secondary emission of evaporated metallic layers at 293° and 83°K . R. Suhrmann and W. Kundt

(*Z. Physik*, 1943, **121**, 118—132).—Layers of Cu, Ag, Au, Cd, and Be are evaporated onto glass in a vac. and then exposed to O_2 for a short time at room temp. The layers are then placed in a vac. and the variation of the secondary emission with the energy of the primary electrons, both at room temp. at liquid air temp. is studied. The yield is only slightly changed in the case of Cu, Ag, and Au at room temp., but at $83^\circ K$. the yield with primary electrons of 100 e.v. increases reversibly by 100% and the max. yield is given for smaller primary electron energy. The effect decreases after several hr. In the case of Be and Cd the yield at room temp. is greatly increased by adsorption of O , but the increase on cooling to $83^\circ K$. is negligible.

L. S. G.

Application of X-ray impulses for the determination of the probability of the attachment of electrons to oxygen molecules. P. Herrng (*Compt. rend.*, 1943, **217**, 135—137).—The principle of the method is to ionise a thin section of the gas in a sealed tube by periodic intense X-ray impulses. Each impulse gives rise to a brief current in the chamber circuit due to the displacement of electrons and positive ions under the action of the field between the electrodes. This current is amplified and studied by means of an oscillograph. Mixtures of A and O_2 were used. The method has the advantage of being direct and involving no hypothesis concerning the rate of decrease of the no. of electrons. The curve of the probability, h , of the taking up of an electron against the kinetic energy of the electrons agrees with that obtained by other workers. The theoretical curve of Bloch *et al.* (A., 1935, 1439) does not show the observed min. and max. The discrepancy is explained qualitatively.

A. J. M.

Velocity distribution of electrons in field-emission. E. W. Müller (*Z. Physik*, 1943, **120**, 261—269).—The velocity distribution of field electrons is calc. on the basis of the tunnel-effect hypothesis and quantitatively computed for a W cathode. Experimental data obtained by the action of an opposing p.d. are in agreement.

Resolving power of the field electron microscope. E. W. Müller (*Z. Physik*, 1943, **120**, 270—282).—The diffuseness of the image produced by the field electron microscope is largely due to variable electronic velocity. The radius of curvature of the emitting point of the cathode and the lateral magnification can be calc. from the emission law and the diffuseness due to velocity variation computed. At high magnifications and small cathodic radii of curvature the effect of diffraction of the electron beam becomes appreciable. The highest resolution so far attained (10 Å.) is limited by cathode surface defects.

L. J. J.

Resolution of the electron microscope for emitting sources. A. Recknagel (*Z. Physik*, 1943, **120**, 331—362).—The electronic emission microscope was replaced by a homogeneous accelerating field and an aberration-free electron lens for calculation of the resolution limit by the Schrödinger wave equation. The effects of spherical and chromatic aberration and wave characteristics on the resolution can be calc. The resolvable dimension is of the order of the wavelength reaching the cathode, and decreases with increasing field strength. The Mecklenburg microscope should give a resolution of $\sim 5 m\mu$. Cutting off the boundary rays does not improve resolution, but makes focussing less crit.

L. J. J.

Apertures of transmission-type electron microscopes using magnetic lenses. L. Marton and R. G. E. Hutter (*Physical Rev.*, 1944, [ii], **65**, 161—167).—Mathematical. Optimum conditions for size and location of apertures are stated for magnetic lenses of the axial field distribution $H(z) = H_0/[1 + (z/\lambda)^2]$. The behaviour of the condenser lens-objective lens system with respect to the angular aperture of the illuminating electron beam is discussed.

N. M. B.

The positive column with a curved discharge path. T. Wasserrab (*Z. Physik*, 1943, **121**, 54—57).—Density distributions are determined in the case where the discharge takes place in the space between two concentric cylinders. The density is given in terms of Bessel functions and the results are presented in graphical form.

L. S. G.

Refractive index of an ionised medium. II. (Sir) C. Darwin (*Proc. Roy. Soc.*, 1943, **A**, **182**, 152—166).—A formula obtained previously (A., 1934, 1137) is confirmed by analysis of the perturbation of the path of an electron by the light during a collision with a proton. The result is believed to be generally true although it is not proved for unsymmetrical charges arbitrarily oriented.

G. D. P.

Origin of the E layer of the ionosphere. J. Gauzit (*Compt. rend.*, 1943, **217**, 179—181).—A mechanism by which a considerable no. of electrons might be produced at an altitude corresponding to the E layer is proposed. Two metastable 1S atoms of O could combine by double collision to form an ionised mol. and an electron. This would give an energy of 13.5 e.v., which is $>$ the energy of ionisation of the mol. formed. The complete mechanism is thus photochemical dissociation of O_2 , excitation by triple collision of the O atoms to the 1S state, and the combination of the 1S atoms with liberation of an electron. This last stage could proceed throughout the night. Ionisation during the night could also be explained by a combination

of the last stage with the mechanism proposed by Martyn *et al.* (A., 1936, 816). There is probably some connexion between the ionisation of the E layer and the intensity of the green line of the night-sky spectrum, since they both depend on the concn. of 1S atoms of O in the upper atm.

A. J. M.

Experiments on and theory of the action of the Geiger point counter. J. Morgan and J. L. Bohn (*J. Franklin Inst.*, 1944, **237**, 371—384).—The relationship between the p.d. of the electrodes and the distance of the point electrode from the end of the cylinder has been investigated for a no. of different cylinders and caps. The relationship between p.d. and counter gas pressure has also been investigated. The efficiency of various points was studied. Unprepared Cu points would not function for $>1-2$ hr. Steel needles ground down to points behaved similarly. A ground steel point did not retain its sensitivity after use but had to be re-ground. Smooth darning needles were the most satisfactory. The theory of the counter is discussed on the basis of Zeleny's view that a high-resistance layer of adsorbed gas exists at the point. It is also assumed that the field at the point at the onset of "self-counting" is sufficient to produce auto-electronic emission. Probability considerations account for selective counting of different ionising agents in certain voltage ranges, for the dependence of counting on the path of ionising rays through the chamber, and for the increase of counts with increase of voltage from the threshold of counting to the point where all rays are registered.

A. J. M.

Polygonal surface and the periodic classification of the elements. G. Haenzel (*Z. Physik*, 1943, **120**, 283—300).—The representation of the periodic system as a series of points on a geometrical surface corresponding with the wave-mechanical characteristics of the elements is described.

L. J. J.

Micro-balance determination of the at. wt. of nitrogen enriched in ^{15}N . K. Clusius and E. Becker (*Z. anorg. Chem.*, 1943, **251**, 92—95).—By means of the micro-balance, an at. wt. of 14.06 has been found for N enriched in ^{15}N by the $NH_4^+-NH_3$ exchange reaction. This corresponds with 5.6% of ^{15}N .

F. J. G.

Masses of ^{35}Cl and ^{37}Cl . A. Gibert, F. Roggen, and J. Rossel (*Portugaliae Physica*, 1944, **1**, 43—46).—The bombardment of Cl. by rapid neutrons gives evidence of a no. of reactions which are difficult to identify. If slow neutrons are used only one reaction occurs, viz., $^{35}Cl + n = ^{36}S + ^1H + q$. The max. val. for the energy, q , of this reaction is 1.16 me.v., and this fixes the upper limit for the mass of ^{35}Cl as 34.98054.

A. J. M.

Spectrography of γ -rays emitted by the active deposit in the slow evolution of radon. L. Salgueiro (*Portugaliae Physica*, 1944, **1**, 67—71).—The results of investigations of the γ -radiation emitted in the transmutation $Ra-D \rightarrow Ra-E$ by absorption, magnetic spectrography, and crystal diffraction are compared. The spectrographic method has been further investigated and γ -rays of λ 267 X. have been detected. Rays of λ 285—295 X., identified by Rasetti and Amaldi, could not be detected after 240 hr. exposure. A new ray, λ 396 X., has been found.

A. J. M.

γ -Rays and the nuclear excitation levels of the active deposit of actinium. J. Surugue (*J. Phys. Radium*, 1942, [viii], **3**, 71—77).—Available data on the radiations of disintegration products of Ac are summarised. γ -Rays from successive disintegrations are analysed and conclusions as to the excitation states of the product nuclei and the nature of the radiations arising from their return to the fundamental state are discussed.

N. M. B.

Behaviour of disintegration recoil particles in a gaseous medium. A. Berthelot and (Mlle.) T. Yuasa (*J. Phys. Radium*, 1942, [viii], **3**, 96—104).—The tracks of recoil products from the disintegration of Ac and Ac-A were studied by the Wilson-chamber method at very low pressure. The at. impact cross-section is 10^{-17} sq. cm. A study of H atom recoil particles gives the velocity-range relation for low-energy protons. The possible role of H_2O micro-drops in various observed phenomena is discussed.

N. M. B.

β -Radiation of actinium. M. Lecoine and (Mlle.) M. Perey (*Compt. rend.*, 1943, **217**, 106—108).—The upper limit of the β -spectrum of Ac, given by Hull *et al.* (A., 1935, 558, 1295) as 220 ke.v., has been re-investigated, using a Wilson chamber at low pressure. At 20 cm. pressure, no β -rays of energy >100 ke.v. were found. Of 1150 tracks, 240 had energy >20 ke.v., 650 had energy between 10 and 20 ke.v., and 240 <10 ke.v. One β -ray is emitted per 12 atoms of Ac disintegrating. The β -rays must be of secondary origin and correspond to an internal conversion of a γ -ray of energy 30—40 ke.v. at the L-level. It is probable that the primary β -radiation from Ac has energy <5 ke.v.

A. J. M.

γ -Radiation of actinium and actinium-K. M. Lecoine, (Mlle.) M. Perey, and S. T. Tsien (*Compt. rend.*, 1943, **217**, 146—148).— γ -Rays emitted from Ac Ac-K are investigated. The absorption curve in Al shows the presence of three groups of rays, γ_A , γ_B , γ_C , of energies 15.6, 36, and 98 ke.v., and relative intensities 140:1:5. When pure Ac-K is used, a similar method shows the existence of only two components of energy 15.3 and 95 ke.v. respectively, the

ratio of intensities being 2 : 1. The intensity of the 95-ke.v. component is ~70% of the intensity of γ_0 , and it is probable that the original γ_0 component arises from Ac-K in the mixture. The γ_A group can be ascribed to the X-ray L-spectra of radio-Ac and Ac-X, disintegration products of Ac and Ac-K. The γ_B group is due to Ac alone. The existence of the weak γ_B group is confirmed by investigating the γ -ray absorption from Ac + Ac-K by various elements of at. no. 48—62. The energy of γ_B is thus found to be 38.8 ± 0.7 ke.v., and absorption experiments with Ac-K, radio-Ac, and Ac-X confirm that it arises from Ac alone. A. J. M.

Absorption of slow neutrons in rare earths and in cadmium. H. Bomke and H. Reddemann (*Z. Physik*, 1942, 120, 56—58).—Effective cross-sections of 13 rare earth elements for thermal neutrons have been determined in very pure preps., giving the vals. Y 4, La 10, Tb 15, Nd 72, Sm 7040, Eu 2700, Gd 22,550, Dy 780, Ho 52, Er 185, Tu 114, Yb 50, Cp 165 sq. cm. $\times 10^{-24}$. The absorption cross-section of Cd for C-neutrons gave the val. 2640×10^{-24} sq. cm. L. J. J.

Activation cross-section of iodine in different forms, with neutrons. F. Knauer (*Z. Physik*, 1942, 120, 103—106).—The effective cross-section of I, for activation by slow neutrons, is the same within 2—3% in I⁻, IO₃⁻, I (solid), and HIO₃ (solid). L. J. J.

Effective cross-sections for absorption of slow neutrons. H. Volz (*Z. Physik*, 1943, 121, 201—235).—Existing methods of measuring effective collision cross-sections with slow neutrons are critically reviewed. A new method is described, in which plane laminae are immersed in H₂O in which a const. concn. of thermal neutrons is maintained. The concn. in the immediate neighbourhood of the surface of the lamina is measured by means of a thin thermal-neutron indicator, and compared with that in the original uniform neutron field. Measurements of the effective collision cross-sections of 49 elements show a completely random distribution of vals. as a function of at. wt. Where the present method gives results differing from earlier vals., the present vals. are nearer those obtained from activity data. An additional absorption process is indicated in only a few cases, e.g., Ta and Bi. L. J. J.

Effective cross-section of technical aluminium for the capture of slow neutrons. J. Gehlen (*Z. Physik*, 1943, 121, 268—284).—The effective cross-section of technical Al for capture of slow neutrons, determined by absorption measurements in paraffin, gives the val. $q_{Al} = 0.43 \pm 0.07 \times 10^{-24}$ cm.², and determined by comparison with the known val. for Ag gives $0.19 \pm 0.02 \times 10^{-24}$ cm.². The half-val. periods for the nuclear processes involved are determined, viz., Ag, short period 33.2 ± 2 sec., long period 148.5 ± 1.5 sec.; Al, 140 ± 2 sec. The ratio of intensities of short to long Ag periods is 3.8 ± 0.6 for saturation with slow neutrons. L. J. J.

Approximation formula for the effective cross-section, σ_{eff} , of slow neutrons for a $1/\nu$ absorber. N. Koyenuma (*Ann. Physik*, 1943, [v], 43, 279—283).—Mathematical. A. J. M.

Preliminary determination of the intensity of a neutron generator. M. Morand and E. Cotton (*Compt. rend.*, 1943, 217, 146—146).—The generator employs bombardment of LiOH by deuterons, and gives an intensity of neutrons equiv. to that from 96 millicuries of Rn + Be. A. J. M.

Neutron emission of the uranium nucleus as a result of its spontaneous disintegration. W. Maurer and H. Pose (*Z. Physik*, 1943, 121, 285—292).—Measurements with 9 kg. of U showed a spontaneous neutron emission with a half-val. period of 2.5×10^{15} years for ²³⁸U. L. J. J.

Spontaneous neutron emission from uranium and thorium. H. Pose (*Z. Physik*, 1943, 121, 293—297).—Measurements of spontaneous neutron emission by U and Th were carried out in a mine in order to avoid cosmic-ray effects. Half-val. periods of 3.1×10^{15} years and 1.7×10^{17} years were found for ²³⁸U and ²³²Th, respectively. L. J. J.

Spontaneous disintegration of uranium and its neighbouring elements. S. Flügge (*Z. Physik*, 1943, 121, 298—300).—For U isotopes, life periods are calc. as 9.1×10^{15} sec. for ²³⁴U, 8.7×10^{20} sec. for ²³⁵U, 8.3×10^{23} sec. for ²³⁸U, giving for the relative activities in normal U 6%, 82%, and 12%, respectively. Th, Io, and Pa give 8.5×10^{25} , 8.1×10^{23} , and 8.9×10^{20} sec., respectively. For elements of mass. no 239, vals. are 8.1×10^{24} sec. for Z = 92, 7.8×10^{20} sec. for Z = 93, and 8.3×10^{16} sec. for Z = 94. L. J. J.

Coefficients of internal conversion in the isomeric transition, $^{80}\text{Br}^* \rightarrow ^{80}\text{Br}$. A. Berthelot (*Compt. rend.*, 1943, 217, 44—46).—1.39 conversion electrons are emitted per transition. This indicates that there are two types of transition involved, two different quanta, of energy 49 and 37 ke.v., being emitted. It is the transition of energy 49 ke.v. which determines the half-life of $^{80}\text{Br}^*$. A. J. M.

Simultaneous emission of two conversion electrons in the isomeric transition $^{80}\text{Br}^* \rightarrow ^{80}\text{Br}$. A. Berthelot (*Compt. rend.*, 1943, 217, 108—110).—The two emissions of energy of 49 and 37 ke.v. (see preceding abstract) are shown to occur simultaneously by the use of coincidence counters. A. J. M.

L 2 (A., I.)

β -Decay. E. J. Konopinski (*Rev. Mod. Physics*, 1943, 15, 209—245).—A comprehensive survey, with bibliography, of theory, with illustrative available data, covering allowed and forbidden spectra and transitions, life times, selection rules, and K capture.

N. M. B.

Production of penetrating showers. L. J. Jánossy and G. D. Rochester (*Proc. Roy. Soc.*, 1943, A, 182, 180—188).—It is shown that about one third of the radiation producing penetrating showers is non-ionising and more penetrating than photons. The intensity of this non-ionising (N-)radiation is ~0.001% of the full cosmic radiation near sea level. It is suggested that the N-radiation consists of neutrons and that it is the energetic part of the penetrating non-ionising component of cosmic radiation. G. D. P.

Anomalous rate of nuclear disintegration effected by cosmic rays. A. P. Zhdanov, N. A. Perfilov, and M. Y. Deisenrod (*Physical Rev.*, 1944, [ii], 65, 202—203).—A preliminary report of disintegrations, reaching 10^3 times the normal rate, observed in the period 23 Nov.—1 Dec., 1942, on unradiated, thickly-coated photographic plates developed 3 days after prep. Possible explanations are suggested. N. M. B.

Method of shower anticoincidences for measuring the meson component of cosmic radiation. V. Sarabhai (*Physical Rev.*, 1944, [ii], 65, 203—204).—A method is described for estimating the intensity of slow mesons which would be liable to be cut out by absorbers filtering the soft electronic component. Preliminary results for various altitudes are reported and discussed. N. M. B.

Spin of the meson. S. K. Chakrabarty and R. C. Majumdar (*Physical Rev.*, 1944, [ii], 65, 206).—Mathematical. N. M. B.

Impact of a wave-packet and a reflecting particle. H. E. Ives (*J. Opt. Soc. Amer.*, 1943, 33, 163—166).—Using only the Newtonian principles of conservation of mass, momentum, and energy and classical wave theory, a general study is made of the impact of wave-packets, i.e., wave-trains of definite length, on reflecting particles, and the variation of mass with velocity is derived. It thus seems probable that all behaviours characteristic of the restricted theory of relativity may be obtained from earlier principles. W. J.

Impact of a wave-packet and an absorbing particle. H. E. Ives (*J. Opt. Soc. Amer.*, 1944, 34, 222—228).—The more complicated problem of an absorbing particle is treated in the same general way as the case of a reflecting particle (see preceding abstract). By considering the production of heat, i.e., kinetic energy of the atoms or sub-particles of which the absorbing particle is composed, and the change of mass of these atoms due to their motion, the overall change of mass of the absorbing particle is obtained, and the equation of motion derived. The present study deals with a stationary absorbing particle, a system in uniform motion, and pressure of radiation on an absorbing particle. B. S. C.

Representation of interactions between neutrons and protons brought about through the intermediary of a particle of spin 2. G. Petiau (*Compt. rend.*, 1943, 217, 103—104).—Mathematical. A. J. M.

Theory of hysteresis curves. A. Hempin (*Compt. rend.*, 1943, 217, 137—139).—Two magnetisation processes are considered: (1) reversible magnetisation, and (2) magnetisation by irreversible displacement of the boundaries separating the areas of influence of Weiss magnetons at 180° to each other. A peculiarity in the Barkhausen effect is discussed. A. J. M.

Finite self-energies in radiation theory. III. A. Lande and L. H. Thomas (*Physical Rev.*, 1944, [ii], 64, 175—184; cf. A., 1942, I, 37).—Mathematical. N. M. B.

II.—MOLECULAR STRUCTURE.

Theory of intensity distribution. [Standardisation of photographs of continuous spectra.] G. Wilkens (*Ann. Physik*, 1943, [v], 43, 73—90).—The conditions necessary for a projected spectrum (e.g., on a photographic plate) to reproduce the true relation of intensity to ν are formulated. A plane projection is unsuitable for intensity measurements on a continuous spectrum. L. J. J.

Application of new analysis of molecular spectra to interesting molecules. Study of a new series of low frequencies. H. Deslandres (*Compt. rend.*, 1943, 217, 92—96).—Published data on infra-red spectra are considered. In the case of 7 mols. investigated at -180° , the low frequencies are simple fractions of the universal const. 1062.5. Three rules are laid down: (1) the mol. can be divided into parts (often only 2), each of which activates the electrons of another part, and the frequency of each part is given by $\nu - qd_1/s'r'$ (s' = no. of activated electrons, $d_1 = 1062.5$, q and r' are integers); (2) the electrons are not activated singly, but in rings, or parts of rings; (3) the ν of the parts are equal or nearly so. The ν of 47 mols. are considered on this basis and satisfactory agreement is obtained. A. J. M.

Flame spectrum of carbon monoxide. III. The cool flame. A. G. Gaydon (*Proc. Roy. Soc.*, 1943, A, 182, 199—206).—Spectra of

cool flames, or pre-ignition glows, of CO with O_2 and N_2O are photographed with small dispersions. The banded structure is more clearly developed in the cool than in the normal flame. The OH bands are absent from the cool flame, which shows strong Na emission. CuCl appears very readily as an impurity and the band systems of CuCl show a different intensity distribution in the cool flames with O_2 and N_2O . The application of the results to the theory of combustion is discussed. (Cf. A., 1941, I, 362.) G. D. P.

New forbidden transition of the neutral nitrogen molecule. (Mme.) R. Herman (*Compt. rend.*, 1943, 217, 141—143).—In the N_2 spectrum there are three band systems, the existence of which indicates that the Lyman bands could be excited by fluorescence. It follows that one of the systems must be forbidden. Bands belonging to a new system, for which the lower state is $a^1\Pi_u$ (the upper state of the Lyman system) and the upper state is at 112781 cm^{-1} (the upper state of the Watson-Kuntz system), contradict the symmetry relation rule. Anomalies arising when a gas is under a moderate pressure are discussed, the Lyman system being entirely modified; the sequences $v'' - v' - 9$ and 10 are extended and the effect attributed at low pressures to dissociation disappears. This is probably due to excitation by ionic collision, and forced emission. A. J. M.

Light absorption of polynuclear inner-complex compounds. IV. Nickel complexes. A. von Kiss and R. Szabó (*Z. anorg. Chem.*, 1943, 252, 172—184; cf. A., 1942, I, 385).—Extinction curves (200—700 $m\mu$.) are recorded for a no. of polycyclic inner-complex Ni compounds. There is no additivity, the absorption curves showing resemblances to those of the org. constituent but little to that of the Ni ion. F. J. G.

Absorption spectra of some hydrated salts of dysprosium. A. M. Rosa (*Ann. Physik*, 1943, [v], 43, 161—181).—The absorption spectra of $Dy_2(SO_4)_3 \cdot 8H_2O$, $Dy(ETSO_4)_3 \cdot 9H_2O$, and $Dy(NO_3)_3 \cdot 5H_2O$ have been investigated. The Stark splitting of the ground term could be obtained only with the sulphate. At liquid-air temp. the components are removed 21 cm^{-1} and 53 cm^{-1} from the lowest component. The intensity of absorption lines produced by superposition of lattice vibrations and electron transitions, and the mean val. of the splitting in the crystal electric field, correspond to the small coupling between the $4f$ -electrons and the crystal lattice. The width of the lines varies considerably within the spectrum. The character of various groups of lines is discussed. A. J. M.

Vibrational spectra of the vinyl halides. P. Torkington and H. W. Thompson (*J.C.S.*, 1944, 303—305).—The infra-red absorption spectrum of $CH_2=CHI$ has been measured between 3 and 20μ . Infra-red and Raman ν have been correlated, the contours of the infra-red bands examined, and magnitudes assigned to the 12 fundamental ν . Variation in magnitude of the various modes with the mass of the halogen atom in these halides is discussed. With three exceptions, the frequency of a given vibration decreases as the mass of the halogen atom increases. W. R. A.

Ultra-violet absorption spectra of solutions of yohimbine, corynanthine, corynantheine, and some of their derivatives. R. Goutarel and A. Berton (*Compt. rend.*, 1943, 217, 71—72).—The mol. extinction coeffs. of these alkaloids and some of their derivatives have been determined in 0.0005M. solution in EtOH at 95° . The spectra of yohimbine and corynanthine are almost identical. There is a min. in the extinction coeff. at $\lambda 2480\text{ A}$. The spectra resemble closely that of cinchonamine, and can be compared with that of indole. Corynantheine shows a displacement towards longer λ , and the min. at 2480 A . could not be observed. The min. does not exist for diacetyl-yohimbine or -corynanthine, although monoacetylcorynanthine shows it. The min. is much less intense for corynantheic acid than for corynanthic acid. The spectra of corynanthic and yohimbic acids are almost identical, and show the same characteristics as those of the alkaloids themselves. A. J. M.

Quinoidation of triaryl compounds [absorption spectra].—See A., 1944, II, 258.

Synthesis and absorption spectra of the ionylideneacetones and related compounds.—See A., 1944, II, 261.

Spectroscopic study in the stereoisomeric capsanthin set. cis-Peak effect and configuration.—See A., 1944, II, 223.

Structure and symmetry of metallic dithionates, deduced from molecular spectra (infra-red absorption and Raman effect). C. Duval and J. Lecomte (*Compt. rend.*, 1943, 217, 42—44).—The absorption spectra of 9 metallic dithionates and 5 complexes containing $(S_2O_6)''$ have been examined over the range 500—1650 cm^{-1} . The strong characteristic absorption bands are at 520, 580, 985, 1200, and 1500—1600 cm^{-1} . The comparison of this spectrum with the Raman spectrum confirms the formula $(S_2O_6)''$ for the radical. It consists of two pyramidal SO_3 groups with a common ternary axis of symmetry, C_2 , on which are placed the two S atoms. There are 6 simple and 6 double degenerate vibrations. The absorption and Raman spectra taken together agree with the symmetry D_{3d} . The usual structural formula for a univalent dithionate, $[MO-S(O)_2]_2$, is not in accord with the spectral data, which indicate no frequency

corresponding to S—O. The SO groups are identical and there is resonance between the O and S atoms. A. J. M.

Raman effect. G. Glockler (*Rev. Mod. Physics*, 1943, 15, 111—173).—A review and bibliography of recent work. W. R. A.

Raman effect. CXLVI. Triatomic and tetratomic molecules (SO_2 , COS, BrCN, BCl_3 , and BBr_3). J. Wagner (*Z. physikal. Chem.*, 1943, A, 193, 55—63).—Polarisation measurements in the Raman spectrum and isotope splitting of Raman lines are recorded. The data correspond to a valency angle of 135° for SO_2 , and agree with a linear mol. for BrCN but not for COS. Data for BCl_3 and BBr_3 agree with a plane centro-symmetric mol. L. J. J.

Raman spectra of dihalogen derivatives of methane, and identification of the nine frequencies of methylene dibromide. (Mlle.) M. L. Delwaulle (*Compt. rend.*, 1943, 217, 172—174).—The polarisations of the Raman lines of CH_2Br_2 , CH_2BrCl , and CH_2BrF have been investigated, and the frequencies assigned to the various mol. vibrations. A. J. M.

Raman spectrum of dimethylnitrosoamine. J. M. G. Barredo and J. Goubeau (*Z. anorg. Chem.*, 1943, 251, 2—13).—The Raman spectrum of $NMe_2 \cdot NO$ has been recorded and the frequencies identified by comparison with those for mols. having comparable structures. The results indicate mesomerism between $NMe_2 \cdot N^+O^-$ and $N^+Me_2 \cdot N^-O^-$. F. J. G.

Excitation of luminous zinc sulphide. M. Curie (*Compt. rend.*, 1943, 217, 110—112).—The brilliance of the luminescence of a no. of substances (particularly ZnS) under conditions of const. excitation agrees with the hypothesis of Riehl (A., 1937, I, 444) that luminosity does not depend on the presence of foreign substances, but that (in the case of ZnS) the exciting radiation is absorbed indifferently by all the Zn atoms, or at least those in a large portion of the lattice perturbed by the presence of a luminous centre. This would not, however, explain the emission of phosphorescence of long duration, which appears only in the presence of a luminogenic impurity. A. J. M.

Viscosity dispersion of dielectric constants of organic liquids for comparatively long waves. P. Mehler (*Ann. Physik*, 1943, [v], 43, 225—243).—A resonance method is used to determine the real dielectric const. (ϵ) of org. substances for waves of λ 15, 60, and 109 m ., and the effect of temp. on ϵ over the range 8— 50° . The viscosity dispersion of ϵ of polar mols. is investigated for $PhNO_2$, $1-C_{10}H_7 \cdot NO_2$, and $MeNO_2$ in a mineral oil (Shell K 20) of high η . The effects of both frequency and temp. show anomalies in the viscosity dispersion. There is good agreement with Debye's theory in the case of the slope and length of the individual dispersion stages for an 11% $PhNO_2$ solution. A. J. M.

Selective heating of small particles in the ultra-short-wave condenser field. H. Schaefer and H. Schwan (*Ann. Physik*, 1943, [v], 43, 99—135).—The heating of small suspended particles in a medium with different electrical properties, under the influence of ultra-short wave fields, is discussed theoretically for stationary and non-stationary temp. conditions. Excess temp. in the dispersed particles are significant only when the conductivity is \gg that of the medium, and in the favourable case of H_2O -in-oil suspensions has a max. val. of 60° at 5—10 kv. per cm. for particles 2 mm. in diameter. A selective particle breakdown by boiling is thus possible. Experimental data obtained with the condenser of a powerful transmitter at λ 11 m. are in agreement. For microscopic and colloid particles, excess temp. are $\ll 0.001^\circ$. L. J. J.

Constitution of compounds of the type SR_2X_2 , SeR_2X_2 , and TeR_2X_2 . K. A. Jensen (*Z. anorg. Chem.*, 1943, 250, 245—256).—Dipole moments are recorded as follows: $(CH_3Ph)_2Si_2$, 4.4; $SePh_2Cl_2$, 3.21; $SePh_2Br_2$, 3.40; $(p-C_6H_4Me)_2TeCl_2$, 2.98; $(p-C_6H_4Me)_2TeBr_2$, 3.21; $[(p-C_6H_4Me)_2TeCl_2]_2O$, 6.1; $TeCl_4$, 2.57 d. The results indicate that in compounds SR_2X_2 ($X = \text{halogen}$) and their analogues the halogen atoms are equiv. and their linkages strongly polar with an electron density of ~ 1 electron. This is illustrated by resonance formulae. The suggested space configuration is a trigonal bipyramid with the fifth point occupied by a lone electron-pair. A compound $(CH_2Ph)_2Si_2$ is described. F. J. G.

Spatial configuration of compounds of the type PR_3X_2 , AsR_3X_2 , SbR_3X_2 , and BiR_3X_2 . K. A. Jensen (*Z. anorg. Chem.*, 1943, 250, 257—267).—The mol. polarisation of $SbPh_3Cl_2$ and $BiPh_3Cl_2$ in C_6H_6 is independent of temp. They have zero dipole moment but unusually large at. polarisation, consistent with the configuration of a trigonal bipyramid, and with the linkages between the central atom and Cl being strongly polar. $SbPh_3(OH)_2$ also has $\mu = 0$; for $BiPh_3(NO_3)_2$, $\mu = 3.26$ d. The Raman spectrum of $SbCl_5$ has six interferences, corresponding with a trigonal bipyramidal configuration. NPh_3Cl has $\mu = 8.20$ d. F. J. G.

Dipole moments of the higher isologues of the sulphoxides and amine oxides. K. A. Jensen (*Z. anorg. Chem.*, 1943, 250, 268—276).—Vals. of μ are recorded as follows: $SePh_3O$, 4.44; $(p-C_6H_4Me)_2TeO$, 3.93; PPh_3O , 4.31; PPh_3S , 4.74; PPh_3Se , 4.83;

PPh_3NPh , 4.45; AsPh_3O , 5.50; SbPh_3S , 5.40; $(p\text{-C}_6\text{H}_4\text{Me})_3\text{SbO}$, 2.0; $\text{PPh}_3\text{O}\cdot\text{H}_2\text{O}$, 4.56; $\text{AsPh}_3\text{O}\cdot\text{H}_2\text{O}$, 5.81; $\text{AsPh}_3\text{Cl}\cdot\text{OH}$, 9.2; $\text{SbPh}_3\text{Cl}\cdot\text{OH}$, 2.8 D. The constitutions of these compounds are discussed.

F. J. G.

Dielectric constants and dipole moments of acetylenic ethers. T. L. Jacobs, J. D. Roberts, and W. G. MacMillan (*J. Amer. Chem. Soc.*, 1944, **66**, 656—657).—Dielectric const. (determined by the heterodyne beat method) and dipole moments (calc. by Onsager's equation) at 25° for $\text{CH}_3\text{C}\equiv\text{OR}$ are $\text{R} = \text{Et}$ 8.05, 1.98, Bu 6.62, 2.03, and Ph 4.76, 1.141, and $\text{CPh}\cdot\text{CH}$ 2.98, 0.78, respectively. High vals. of μ for the alkyl ethers may be due to contributions from resonance forms of the type $\text{CH}^+\text{C}\equiv\text{OR}^-$. Onsager's equation is fairly accurate for $\text{CPh}\cdot\text{CH}$, PhOMe , PhOEt , Ph_2O , and Pr_2O , but not for Et_2O (cf. Bottcher, A., 1939, I, 126).

R. S. C.

Influence of polarisation on electric breakdown strength and its dependence on temperature. G. Malmlov (*Arkiv Mat. Ast. Fys.*, 1944, **30**, B, 8 pp.).—Apparatus and methods for measuring the breakdown strength are described and measurements are made on mica and KBr with d.c. and a.c. The results show that the vals. obtained with d.c. are influenced by polarisation. The electric breakdown strength of KBr is independent of temp. between 220° and 300° K.

L. S. G.

Refractive indices in the ultra-violet. M. Bayen (*J. Phys. Radium*, 1942, [viii], **3**, 57—68).—An improved method of determination is described, and data for H_2O , $^2\text{H}_2\text{O}$, and aq. solutions of NaCl are tabulated. A discussion of results for electrolytic solutions with reference to extinction coeffs. and mol. refraction shows that the deformation of ions increases with the concn.

N. M. B.

"Detachment" of optical activity and absorption. R. Servant (*J. Phys. Radium*, 1942, [viii], **3**, 90—96).—The distinction, in an absorption band, between the "active" part and the whole band is discussed with reference to available data, theories, and interpretations. Typical illustrations are given by quartz.

N. M. B.

Relation of the dispersion of refraction in the infra-red to that in the visible and ultra-violet. L. Amy (*Compt. rend.*, 1943, **217**, 227—229).—The curve representing the variation of n^2 as a function of $\log \lambda$ is symmetrical. A new formula giving the dispersion of n is proposed.

A. J. M.

Orientation of molecules at boundary surfaces and in associated molecules by electrostatic forces. H. Dunken (*Z. physikal. Chem.*, 1943, A, **193**, 40—54).—Theoretical. Mutual orientation of dipoles and quadrupoles and their arrangement at metallic boundary surfaces are discussed, and the corresponding effect in adsorption is considered.

L. J. J.

Characteristic frequency of double bonds in conjugated systems. A. Kirrmann (*Compt. rend.*, 1943, **217**, 148—150).—The lowering of the characteristic frequency due to the double bond when it is conjugated is not a general phenomenon. Deviations can be explained on the basis of mesomerism.

A. J. M.

Linear flow of perfect gases. J. Villey (*J. Phys. Radium*, 1942, [viii], **3**, 79—80).—Mathematical.

N. M. B.

Energy- and order-states of the atoms in the surfaces of liquids and solids. R. Haul (*Z. physikal. Chem.*, 1943, B, **53**, 331—361).—Theoretical. The relation of surface energy (γ) to the heat of sublimation or vaporisation is discussed. With He, Ne, Ar, Hg, Na, Pb, Ag, and Au as examples of simple liquids, conclusions are drawn as to the arrangement of the surface atoms. From crystallographic considerations, the total surface energy (Σ) of the above elements in the solid state is calc., for various temp. and crystal faces, from the internal heat of sublimation. A method is given for determining the temp. coeff. of γ for solids. The surface entropy so obtained can be used to calculate γ from Σ . As no reliable experimental method is available for the determination of γ for solids, theoretical methods must be used.

J. F. H.

Cross-sectional areas of molecules adsorbed on solid surfaces.—See A., 1944, I, 199.

III.—CRYSTAL STRUCTURE.

Diffraction of X-rays by quartz in supersonic vibration. J. Surugue and T. T. Ouang (*Compt. rend.*, 1943, **217**, 177—179).—When quartz is set into supersonic vibration the intensity of the Laue spots is increased (Fox *et al.*, *Physical Rev.*, 1931, [ii], **37**, 1622). This phenomenon is reinvestigated. The relative increase in intensity is \propto voltage applied to the quartz, and therefore \propto the amplitude of the vibrations. The explanation is discussed.

A. J. M.

Ambiguities in the X-ray analysis of crystal structures. A. L. Patterson (*Physical Rev.*, 1944, [iii], **65**, 195—201).—The problem of uniqueness in the X-ray analysis of a crystal structure depends on the uniqueness of the determination of the arrangement of a periodic set of points in space by its vector distance set. A large no. of cases is presented in which 2, 3, or 4 non-congruent sets of points

are homometric, i.e., have the same vector distance set. The significance of these results for practical crystal analysis is discussed.

N. M. B.

Character tables for two space-groups. C. Herring (*J. Franklin Inst.*, 1942, **233**, 525—543).—Character tables (irreducible representations of the space-group) are given for the close-packed hexagonal and the diamond type lattice, in which no point of space possesses the symmetry of the point group.

A. J. M.

Crystal forms of tungsten in growth and decay and the direct-current effect. R. W. Schmidt (*Z. Physik*, 1942, **120**, 69—85).—W crystals grow in the form of rhombic dodecahedra. Octahedra are produced by etching with alkaline $\text{K}_3\text{Fe}(\text{CN})_6$. The (110) faces have the greatest speed of dissolution in $\text{HF}\text{--}\text{H}_2\text{SO}_4$ mixtures. Recrystallisation in drawn wires gives layers $\sim 1 \mu$ thick, parallel to one of the cubic planes of W. The d.c. effect is due to the wandering of ions, and leads to a building up of regular steps on the (111) regions, and to a smaller extent on the (110), but not at all on the (100). The steps have a max. size of $\sim 15 \mu$ at 2400° K., and diminish in size with temp.

L. J. J.

Thomson-Gibbs equation and the so-called theory of growth conglomerates. I. N. Stranski (*Z. Krist.*, 1943, **105**, 91—123).—The Thomson-Gibbs equation is deduced and its applications are discussed. In particular the work of Balarev is criticised as being founded on erroneous applications of the equation.

A. J. M.

Wulff's law for the equilibrium form of crystals. M. von Laue (*Z. Krist.*, 1943, **105**, 124—133).—Various deductions of Wulff's law are discussed, including thermodynamic methods.

A. J. M.

Oriented growth of quinol on mica. J. Willems (*Z. Krist.*, 1943, **105**, 144—148).—When solutions of α -quinol (I) in solvents of low dielectric const. (e.g., C_6H_6 and CHCl_3) crystallise on a mica surface, the crystals are oriented in definite directions. As in other cases (A., 1944, I, 99) this appears to be due to a H bond between the O of (I) and O of the mica. The oriented growth of (I) on mica is of particular interest since succinic acid, of which the lattice dimensions are more favourable for this growth, does not behave in the same way.

A. J. M.

Oriented growth of quinol on heavy spar and celestine. J. Willems (*Z. Krist.*, 1943, **105**, 155—156).—The conditions necessary for oriented growth of quinol (crystal type C_{2d}) from solvents of low dielectric const. are present in the case of heavy spar and celestine. Oriented growth of α -quinol from C_6H_6 has been observed on the (001) surfaces of the above minerals.

A. J. M.

Oriented growth of urotropin on gypsum. Forces involved in the oriented growth of crystals of organic substances. J. Willems (*Z. Krist.*, 1943, **105**, 149—154).— $(\text{CH}_3)_3\text{N}_4$ (I) crystallises on the (010) surface of gypsum (II) with (110) of (I) parallel to (010) of (II), and [110] of (I) parallel to [301] of (II). The forces involved in the production of oriented growth are discussed. In this case there is probably a combination of van der Waals forces with homopolar linkings, either between (I) and the ions of CaSO_4 , or with the H_2O .

A. J. M.

Lattice constants and expansion coefficients of iodine. M. Straumanis and J. Sauka (*Z. physikal. Chem.*, 1943, B, **53**, 320—330).—The lattice const. of I were determined at 10—40° by the rotating-crystal method. At 18° $a = 4.7761$, $b = 7.2501$, $c = 9.7711$ Å. Linear expansion coeffs. parallel to the axes a , b , and c are 133.4×10^{-6} , 95×10^{-6} , and 35.1×10^{-6} respectively; hence the cubic expansion coeff. is 264×10^{-6} . At 18° $\rho = 4.9520$, in best agreement with the results of Gay-Lussac (*Ann. Chim. Physique*, 1814, **91**, 7) and Stas (*Mém. Acad. Belg.*, 1865, **35**, 3). Although the crystals of I were prepared at 27—30° and 70—80° only rhombic I was obtained, indicating that the transition point of Kurbatow (A., 1908, ii, 31) does not exist.

J. F. H.

Crystal structure of cadmium iodide. G. Hagg and E. Hermansson (*Arkiv Kemi, Min., Geol.*, 1943, **17**, B, No. 10, 4 pp.).— CdI_2 has a C27 structure if cryst. slowly from solution. If cryst. quickly (e.g., from SO_2 or MeOH at ordinary pressure or from H_2O , EtOH, or COMe_2 under reduced pressure) a random layer structure is obtained. At intermediate rates of crystallisation disordered structures giving powder photographs corresponding with a C6 structure are obtained. If cryst. from a melt a C27 structure is obtained even at high crystallisation rates.

C. R. H.

Crystal structures of SrMg_2 , BaMg_2 , and CaLi_2 . E. Hellner and F. Laves (*Z. Krist.*, 1943, **105**, 134—143).—The existence of compounds SrMg_2 , BaMg_2 , and CaLi_2 is demonstrated. They crystallise in the MgZn_2 type, with the following lattice const.: SrMg_2 , a 6.426, c 10.473 Å., c/a 1.628; BaMg_2 , a 6.636, c 10.655 Å., c/a 1.606; CaLi_2 , a 6.248, c 10.23 Å., c/a 1.637. The at. separation in CaLi_2 is somewhat $>$ in CaMg_2 , although the Li atom is smaller than Mg in the elementary state. The apparent radii of Li, Mg, Ca, Sr, Ba, Al, La, and Ce in this type of compound are discussed. The rule that $R_A/R_B = (1.5)^{1/2}$ (R_A , R_B are at. radii of A and B in the compound AB_2) holds fairly well for these compounds. Deviations from this

rule found by Nowotny (*Z. Metallk.*, 1942, **34**, 247) for the types MgCu_2 , MgZn_2 , MgNi_2 , and CeNi_2 are due to the erroneous use of the radii of the atoms in the elementary state. A. J. M.

Configurations of a binary mixed crystal. R. Eisenschitz (*Physical Rev.*, 1944, [ii], **65**, 204—205).—Mathematical. An alternative treatment of the work of Ashkin and Lamb (cf. A., 1944, I, 6).

N. M. B.

X-Ray studies on oxides and oxyhalides of trivalent bismuth. L. G. Sillen (*Dissert., Stockholm*, 1940, 140 pp.).—A complete account of researches already recorded (A., 1938, I, 501, 560; 1939, I, 412, 457; 1940, I, 349; 1941, I, 153, 246; 1942, I, 46, 136, 269, 260; 1943, I, 67, 146, 129). A. J. M.

X-Ray analysis of FeSn_2 and Fe_3Sn . O. Nial (*Arkiv Kemi, Min., Geol.*, 1943, **17**, B, No. 11, 5 pp.).— FeSn_2 belongs to the space-group D_{2h}^{18} — $I4/mcm$ with lattice const. (± 0.003) a 6.520, c 5.312 Å. It is isomorphous with CoSn_2 and MnSn_2 , the const. for the latter being a 6.646, c 5.425 Å. Fe_3Sn belongs to the space-group D_{6h} — $C6/mmc$ with a 5.447, c 4.352 Å, and is isomorphous with Ni_3Sn . C. R. H.

X-Ray studies on ABO_4 compounds of rutile type and AB_2O_6 compounds of columbite type. K. Brandt (*Arkiv Kemi, Min., Geol.*, 1943, **17**, A, No. 15, 8 pp.).—The prep. of numerous compounds of rutile and columbite structures is described. X-Ray examination gives the following lattice const. (a and c respectively in Å.): CrTaO_4 4.626, 3.009; FeTaO_4 4.672, 3.042; RhTaO_4 4.684, 3.020; CrNbO_4 4.635, 3.005; FeNbO_4 4.688, 3.05; RhNbO_4 4.686, 3.014; AlSbO_4 4.510, 2.961; CrSbO_4 4.577, 3.042; FeSbO_4 4.623, 3.011; RhSbO_4 4.601, 3.100; GaSbO_4 4.59, 3.03; RbVO_4 4.607, 2.923; MgNb_2O_6 5.017, 5.665; NiNb_2O_6 5.013, 5.661; CoNb_2O_6 5.036, 5.701; FeNb_2O_6 4.992, 5.616; ZnNb_2O_6 5.036, 5.715; MnNb_2O_6 5.081, 5.766; ZnTa_2O_6 5.058, 5.682; MnTa_2O_6 5.092, 5.750; MnSb_2O_6 5.106, 5.736; columbite 5.082, 5.730. The first twelve of these compounds have space-group D_{2h}^{14} — $P4/mmm$ (rutile structure); the remainder have the columbite structure. C. R. H.

Structure of transparent soap. J. W. McBain and S. Ross (*Oil and Soap*, 1944, **21**, 97—98).—The similar X-ray diffraction patterns of a 20-year-old and of a fresh sample of Pears' transparent soap prove that the soap has not a glassy or amorphous structure as has been hitherto supposed, but consists of ultra-microscopical crystallites arranged completely at random. The Bragg spacings resemble those of the most stable cryst. form (the γ -form, also termed ω -form by Ferguson *et al.*; A., 1943, I, 306) of a Na soap at room temp. The pattern of glycerol (typically a liquid or amorphous glass) is also visible. E. L.

Space lattice of codeine and β -methylmorphimethine. L. Castelliz and F. Halla (*Z. Krist.*, 1943, **105**, 156—157).—Codeine (I) has a 27.70, b 29.80, c 7.59 Å; 16 mols. in the unit cell; space-group V^2 — $P2_12_12$. β -Methylmorphimethine has a 16.88, b 29.60, c 12.90 Å; 16 (~ 17) mols. in the unit cell; same space-group as (I). The relation between the two cells appears to be that the cell of one is divided into two, and the halves are reunited in another direction. A. J. M.

Phenylcarbamyl derivatives of alkylated phenols. M.p. and X-ray powder diffraction data.—See A., 1944, II, 256.

Suitability of poorly bound photolayers for use in the electron microscope. M. von Ardenne (*Z. Physik*, 1943, **121**, 1—6).—Such photolayers are considered with reference to the conditions existing in the electron microscope and they are found to be quite suitable. L. S. G.

Electron diffraction by amorphous polymers. D. G. Coumoulos (*Proc. Roy. Soc.*, 1943, **A**, **182**, 166—179).—The diffraction patterns of the polyvinyl acetate and the acrylate and methacrylate polymers suggest a zig-zag C-atom chain with the side-chains alternately to the right and left of the zig-zag chains and in planes approx. perpendicular to the main chain. These side-chains are subject to lateral cohesive forces which group them into clusters. In films, prepared by evaporation of a solution on a H_2O surface, the clusters consist of a small no. of side-chains without any special orientation. With multilayers, prepared by the usual technique, some orientation of the side-chains is indicated. The patterns indicate an amorphous character which is attributed to the tendency of the side-chains to close packing in clusters, producing distortion of the main chain. The elastic properties of the polymers are discussed. G. D. P.

Electron diffraction investigation of monomerides and dimerides of formic, acetic, and trifluoroacetic acids and the dimeride of deuterium acetate. J. Karle and L. O. Brockway (*J. Amer. Chem. Soc.*, 1944, **66**, 574—584).—The electron diffraction of monomerides and dimerides of HCO_2H (I), AcOH (II), and $\text{CF}_3\text{CO}_2\text{H}$ (III) and of the dimeride of AcOD (IV) has been determined. A nozzle, independently heated to $\sim 160^\circ$, has been used for the monomeride photographs. Parameter vals. are: (I), $\text{C—O} = 1.42$ Å, $\text{C=O} = 1.24$ Å, angle $\text{O—C—O} = 117^\circ$; (II), $\text{C—O} = 1.36$ Å, $\text{C=O} = 1.25$ Å, $\text{OH—O} = 2.73$ Å, angle $\text{O—C—O} = 121^\circ$, angle $\text{C}\cdots\text{C}=\text{O} = 58^\circ$; (III), $\text{C—O} = 1.43$ Å, $\text{C=O} = 1.24$ Å, $\text{C—C} = 1.54$ Å, angle $\text{O—C—O} = 122$ — 138° , angle $\text{C—C—O} = 113$ — 128° ; (IV), $\text{C—O} = 1.36$ Å, $\text{C=O} = 1.25$ Å, $\text{OH—O} = 2.76$ Å, $\text{C—C} = 1.54$ Å, angle $\text{O—C—O} =$

130° , angle $\text{C}\cdots\text{C}=\text{O} = 60^\circ$; (III), $\text{C—F} = 1.36$ Å, angle $\text{F—C—F} = 110^\circ$; (II), $\text{C—F} = 1.36$ Å, $\text{C—C} = 1.47$ Å, $\text{OH—O} = 2.76$ Å, mean of C—O and $\text{C=O} = 1.30$ Å, angle $\text{F—C—F} = 109^\circ$, angle $\text{O—C—O} = 130^\circ$, angle $\text{C}\cdots\text{C}=\text{O} = 60^\circ$. Quantitatively identical parameters have been obtained for the dimerides of (II) and (IV). Approx. measurements have been made of the v.d. and dissociation const. of the dimeride of (III). These vals. of the parameters show that the C—O bonds differ in both monomeride and dimeride, and that the H atoms are not symmetrically placed with respect to the OH—O bonds. The CF_3 group in (III) is free to rotate or oscillate with a large amplitude about the C—C axis. W. R. A.

Structures of methylenecyclobutane and of 1-methylcyclobutene. W. Shand, jun., V. Schomaker, and J. R. Fischer (*J. Amer. Chem. Soc.*, 1944, **66**, 636—640).—Methylenecyclobutane (I) and 1-methylcyclobutene (II), prepared from pentaerythritol tetrabromide, have the following properties; (I), b.p. = $41.39^\circ/750$ mm., $n_D^{20} = 1.4266$, 1.4236 , 1.4210 , $p_D^{20,25} = 0.7401$, 0.7349 ; (II), b.p. = $37.1^\circ/750$ mm., $n_D^{20} = 1.4088$, $p_D^{20,25} = 0.7244$, 0.7188 . Electron diffraction of (I) and (II) confirms the previously postulated structures; with: (I), $\text{C—C} = 1.55 \pm 0.02$ Å, $\text{C=C} = 1.34 \pm 0.03$ Å, and angle $\text{C}_2\text{—C—C}_2 = 92.5 \pm 2^\circ$ (C carrying the CH_2 group); (II), $\text{C—C} = 1.54 \pm 0.03$ Å, $\text{C=C} = 1.34 \pm 0.03$ Å, angle $\text{C}_2\text{—C—C}_2 = 125 \pm 4^\circ$ (the double bond lying between C and C_2). W. R. A.

Residual magnetostriction of polycrystalline iron and nickel. M. Kornetzki (*Ann. Physik*, 1943, [v], **43**, 203—219).—The theory of magnetostriction remanence is discussed. For a slightly strained polycrystal with a cubic lattice there are always some crystallographically equiv. directions which are more readily magnetised than others. From the connexion between magnetisation and magnetostriction it is shown that there are two distinct cases of magnetostriction remanence. The first corresponds to the example where an isotropic substance has a magnetic remanence of 50% of the saturation magnetisation, the magnetism being taken up in the state of lowest energy. There is no magnetostriction remanence in this case. The other corresponds to a magnetic state of higher energy, and a magnetic remanence of $\sim 83\%$. Here the magnetostriction remanence amounts to about half the saturation val. of a single crystal in the direction of easiest magnetisation. The softness of the crystal will affect the magnetostriction remanence. The determination of magnetostriction of Fe and Ni wires with a small shearing factor shows that soft samples have considerable remanence, amounting to 40—50% of the saturation val. A considerable portion of the magnetisation does not go into the position of lowest energy. Hard Ni has only a small magnetostriction remanence. The magnetostriction is discussed in connexion with resistance changes in a magnetic field. A. J. M.

Crystal-optical constants of organic dyes. Polymorphism of dyes caused by solvents. III. I. Riskin (*J. Appl. Chem. Russ.*, 1943, **16**, 201—205).—1:2- p - $\text{NO}_2\text{C}_6\text{H}_4\text{N:N}(\text{C}_{10}\text{H}_7)\text{OH}$ forms dark red crystals from PhMe and orange-red crystals from quinoline (or, in some conditions, from $\text{C}_6\text{H}_5\text{N}$). Hansa-yellow 3R (constitution unknown) gives orange and yellow crystals from PhMe and $\text{C}_6\text{H}_5\text{N}$, respectively. The optical const. of these crystals are given.

Hardness of metals in relation to atomic structure. H. O'Neill (*Metallurgia*, 1944, **29**, 243—247).—In pure metals, indentation hardness corresponds generally with the reciprocal elastic compressibility when both are plotted against at. no.; exceptions can be attributed to complex crystal structures. The influence of valency electrons and of variations in the nature of at. linkings in metallic alloys is briefly discussed. J. C. C.

Structural premises of strain-hardening and precipitation. C. H. Mathewson (*Trans. Amer. Soc. Met.*, 1944, **32**, 38—87).—Campbell memorial lecture. An account is given of existing theories of the nature of slip and twinning in metals. The Taylor theory of fault propagation fails to explain the formation of wide twin lamellæ on straining Zn, Sn, Fe, and some other metals, and to account for the variations between metals of the same crystal form in their susceptibility to work-hardening. A modification of the slip-interference theory of strain-hardening is advanced in which slip is considered to be far more complicated than is usually assumed and to follow a devious course in which the atoms find paths of lower potential than the direct route over barriers set up by their own vol. requirements. Measurements (by W. R. Hibbard) of the slip and rotation of the grains in tensile specimens of Cu, (by J. A. Collins) of the lattice rotation of crystallites in a strained single crystal of Al, and (by R. G. Treuting) of the axis shift of the grains in α -brass and Al (*Yale Diss.*, 1942, 1939, and 1942) are described and shown to be in accord with theory. J. C. C.

Manner of nucleus formation of new phases. I. N. Stranski (*Z. Ver. deut. Ing., Beih. Verfahrenstechn.*, 1941, 39—43; *Chem. Zentr.*, 1942, I, 407).—Volmer's formula for the frequency of nucleus formation is discussed, and the nature of crystal nuclear formation of new phases is examined with reference to some examples of growth of rounded single crystals. R. B. C.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

New attempt to interpret the Meissner-Ochsenfeld effect, and the nuclear theory of superconduction. K. M. Koch (*Z. Physik*, 1942, 120, 86—102).—The Meissner-Ochsenfeld effect can be explained on the assumption that superconduction depends on the formation of growth centres which are formed spontaneously below a crit. temp. The question whether such centres participate in normal conduction is discussed. L. J. J.

Law of magnetisation in weak fields. K. Sixtus (*Z. Physik*, 1943, 121, 100—117).—The permeability (μ) is measured for Fe alloys having respectively 3% Si; 40% Ni; 76% Ni, 2% Cr, and 5% Cu (Mumetal), and 20% Cr. The alloys are all first heated to incandescence and the field strength (H) is < 35 oersted. Graphs drawn of μ against H have curvature showing a departure from the Rayleigh law for weak fields, $\mu - \mu_0 + cH$. A generalised law, $\mu = H^a(\mu_0 + C/H)$, where $0 < a < 1$, is proposed; it fits the data over a large range of the field strengths, but not at the lowest vals. This is explained. L. S. G.

Absolute measurement of large magnetic fields by a null method. H. Mikhail and Y. L. Yousef (*Proc. Physical Soc.*, 1944, 56, 249—250).—The condenser method described is based on the simultaneous passage through a fluxmeter of a charge equal and opposite to the charge that would flow if a search coil were removed from the field. N. M. B.

Acoustical tables for air and sea water. W. L. Woolf (*J. Acoust. Soc. Amer.*, 1943, 15, 83—86).—The tables given show the relations between pressure level, sound pressure, intensity level, particle velocity, and particle displacement \times frequency. Equations and other data are presented. N. M. B.

Use of the Pierce interferometer for measuring the absorption of sound in gases. H. C. Hardy (*J. Acoust. Soc. Amer.*, 1943, 15, 91—95).—The empirical Pielemeier equation method, based on the theory of the Pierce interferometer, is justified by a more rigorous treatment of the effect of sound resonance on the oscillator. N. M. B.

Absorption measurements in the ultrasonic region. H. Born (*Z. Physik*, 1943, 120, 383—396).—The existence of interference fields in the neighbourhood of a vibrating quartz crystal has been demonstrated by measurements of the energy distribution with the quartz probe described. A correction function is derived for the elimination of interference effects in absorption measurements. L. J. J.

The Kritschewski-Kazarnovski equation of state for gas mixtures. M. Temkin (*J. Phys. Chem. Russ.*, 1943, 17, 269—270).—The equation (cf. A., 1939, I, 516) can be derived theoretically if the behaviour of the gases does not deviate too much from that of perfect gases. J. J. B.

Thermal repulsion. M. K. Paranjape (*Current Sci.*, 1944, 13, 72—73).—Measurements at 0—1 atm. of the gas surrounding a mica vane suspended between hot and cold faces and subject to thermal repulsion (F) show that F increases only slightly as the pressure falls 71—1 cm. of Hg. Below 1 cm. there is first a gradual and then a very rapid increase in F to a max. of ~ 0.27 dyne per sq. cm. at $\sim 10^{-2}$ cm. of Hg. As the pressure is further reduced F decreases rapidly. N. M. B.

Direct determination of the slip coefficients, s_{44} , s_{55} , for substances of rhombic symmetry and low rigidity. H. Hörig (*Ann. Physik*, 1943, [v], 43, 285—295).—A method of determining the slip coeffs. (Vogt's moduli) directly is described. Results are given for a no. of woods, and are compared with the vals. for steel and celluloid calc. from existing data. A. J. M.

Liquid state. J. H. Hildebrand (*Proc. Physical Soc.*, 1944, 56, 221—239).—Guthrie lecture. N. M. B.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Theory of diffusion of binary mixtures and interpretation of diffusion measurements. O. Lamm (*Arkiv Kemi, Min., Geol.*, 1943, 17, A, No. 9, 21 pp.).—Mathematical. The theory of unidimensional diffusion has been developed for the general case of a homogeneous two-component mixture. C. R. H.

Diffusion of highly concentrated salt solutions: potassium fluoride in water. O. Lamm (*Z. anorg. Chem.*, 1943, 250, 236—244).—Vals. of D and η for KF in H_2O over the concn. range 34—48% are recorded. The product $D\eta$ is $\sim 5 \times 10^{-7}$ c.g.s. F. J. G.

Diffusion equations, their representation by models, and diffusion experiments on silicic acid gels. II. Diffusion in a confined space with constant initial concentration. A. Dobrowsky (*Kolloid-Z.*, 1943, 105, 56—70).—The general solution of the diffusion equation is developed and applied to the cases of diffusion from a cylinder open at one end, and open at both ends, the initial concn. being const. throughout the cylinder. The mathematical treatment leads to expressions for the concn. at any point after a given time, the quantity diffusing through any section, and the quantity diffusing out of the cylinder. Experiments are carried out on silicic acid gels,

prepared by acidifying water-glass solutions, the diffusing substance generally being $Na_2Cr_2O_7$. Gels have advantages over liquids for diffusion experiments. Diffusion from the sides of the cylindrical gels was prevented by immersing them in xylene and exposing only the ends to H_2O . The formulæ could be verified by analysing sections of the cylinders after diffusion had taken place. The evaluation of the diffusion coeff. from the resulting curves is described. The phenomena can also be simulated by a hydraulic model. R. H. F.

Rapid method for the determination of Ludwig-Soret coefficients. N. Riehl (*Z. Elektrochem.*, 1943, 49, 306—309).—The hot solution is contained in a vessel into which dips a cylinder either made of thick glass or constructed as a Dewar vessel. This cylinder is closed at the bottom by a Cellophane membrane and contains the cold solution in which is immersed a Cu cooling coil. With this apparatus temp. differences of 60° can be attained. With 0.1N-KOH equilibrium is attained in $\sim 2\frac{1}{2}$ hr. and the Ludwig-Soret coeff. deduced is in accord with previous data. With $BaCl_2$ the time required for establishment of equilibrium is much longer and the coeff. deduced from the results is the previously reported val. (Chipman, A., 1926, 1206). It is suggested that many recorded vals. of this coeff. are too low owing to the mixing of the solutions. J. W. S.

Variation with temperature of the velocity of sound in mixtures of water and methyl alcohol. G. Goudet (*Compt. rend.*, 1943, 217, 65—68).—The coeff. $\mu = -(1/\rho)(d\rho/d\theta)$ (ρ = velocity of sound, θ = temp.) is positive for all liquids except H_2O . It should therefore be possible to obtain a mixture of H_2O and another liquid for which $\mu = 0$. For this purpose, the velocity of sound in mixtures of H_2O and MeOH has been determined at $\sim 30^\circ$. A direct method of measuring μ using ultrasonic waves is described. μ is zero for a mixture of 30 c.c. of MeOH with 100 c.c. of H_2O . A. J. M.

Hygroscopicity, properties in boric acid solution, and specific viscosities of mixtures of diastereoisomeric butane- β -diols. T. M. Lees, E. I. Fulmer, and L. A. Underkofler (*Iowa Sta. Coll. J. Sci.*, 1944, 18, 359—367).—The prep. of *meso*-(CHMeOH) $_2$ from the mixture produced by the action of *Aerobacter aerogenes* on glucose is described. Both this and the *l*-glycol are extremely hygroscopic. Sp. viscosities of mixtures of the *meso*- and *l*-forms at 30° give a continuous curve, the val. of η for the *meso*- being 3 times that for the *l*-glycol. Sp. conductivities (κ) of 10% solutions of mixtures in 0.5M- H_3BO_3 at 25° , and their pH vals., are recorded. κ is the higher, and pH the lower, the greater is the proportion of the *l*-glycol in the mixture. The κ measurements offer a convenient method of analysis of mixtures containing *meso* and active forms. F. L. U.

Cryoscopic constant of camphor. J. E. Ricci (*J. Amer. Chem. Soc.*, 1944, 66, 658—658).—Deviation of the cryoscopic const. of camphor from constancy below 0.2M-solute, observed by Meldrum *et al.* (A., 1944, I, 33), is considered to be due to a decrease in the m.p. of the camphor on melting and grinding. 0.005M. concn. of impurity formed during this process would result in a hyperbolic deviation of the observed magnitude. W. R. A.

Density of melts in the system boric oxide-silica. A. A. Leontieva (*J. Phys. Chem. Russ.*, 1943, 17, 264—268).— d of 5 melts between B_2O_3 100 and B_2O_3 85, SiO_2 15 wt.-% is determined between 530° and 1325° . Although d was expected to be additive, it shows max. at B_2O_3 98, SiO_2 2%; at $[SiO_2] > 10\%$ the deviation from additivity is small. The coeff. of thermal expansion increases with $[B_2O_3]$. J. J. B.

The α -($\alpha + \gamma$) phase boundary in the copper-beryllium system. H. Borchers and H. J. Otto (*Metallwirts.*, 1942, 21, 215—217).—Six alloys containing 0.3—2.45% of Be were investigated dilatometrically, and it was found that the α -($\alpha + \gamma$) boundary occurred at 379° , 466° , and 600° , in alloys containing 0.3, 0.7, and 1.0% Be, respectively. The α -($\alpha + \beta$) boundary in the higher-Be alloys could not be determined as the effects observed were too small. C. E. H.

Influence of various elements on the position of the eutectoid in the iron-carbon (carbide) system. C. L. Shapiro and J. Strauss (*Amer. Inst. Min. Met. Eng.*, 1943, *Tech. Publ.*, 1646, 19 pp.; *Met. Tech.*, 10, No. 8).—Elements which form definite carbides with Fe increase the [C] of the ternary eutectoid. These comprise Al, Be, Nb, Ta, Ti, V, and Zr and are termed class I elements. Class II elements, Co, Cu, and Si, form no carbides, enter into solid solution with Fe, and shift the eutectoid to a lower [C]. Mo, which first forms solid solutions with Fe and then, in higher concns., forms carbides which undergo peritecto-eutectoid reactions, first decreases and then increases the [C] of the eutectoid. It is suggested that Cr, W, Mn, and Ni, which in lower concns. decrease the [C] of the eutectoid, may behave in the same general manner and, with Mo, comprise class III elements. The conception of peritecto-eutectoid reactions, which result in the formation of three phases (α -Fe, Fe $_3$ C, and compound) and may take place over a range of temp., is discussed. J. C. C.

Passivity in copper-nickel and molybdenum-nickel-iron alloys. H. H. Uhlig (*Trans. Electrochem. Soc.*, 1944, 85, *Preprint* 20, 207—218).—The author's theory, that passivity in an Fe or Ni alloy appears at a crit. composition related to the tendency of a band of electronic energy to fill with electrons (cf. B., 1939, 1046), is tested

by existing data on the passivity of Cu-Ni and Mo-Ni-Fe alloys. It is known that for Cu-Ni alloys the α band is filled at 60 at.-% Cu, and corrosion data confirm that passivity occurs at the same composition. Conditions of electron transfer or sharing described for binary alloys are essentially retained in the Mo-Ni-Fe system. Data for corrosion of the 28, 35, and 60% Ni series in H_2SO_4 confirm the prediction from the theory that passivity will occur at the at. ratio Mo:Fe = 1:5. The theory is similarly confirmed in connexion with the addition of Mo to austenitic stainless steel, and the [Mo] required to passivate the alloy Hastelloy A. C. E. H.

Solubility of ferrous oxide in pure solid iron.—See B., 1944, I, 272.

Organometallic lead and tin compounds. K. A. Jensen and N. Clauson-Kaas (*Z. anorg. Chem.*, 1943, 250, 277—286).—The solubility of hexacyclohexyldiplumbane, $Pb_2(C_6H_{11})_6$, is 1.4% in C_6H_6 and 1.6% in $CHCl_3$ at 30°. Measurement of χ indicates that the solutions are not appreciably dissociated into paramagnetic radicals. $SnPh_2$ is diamagnetic and has an appreciable dipole moment. F. J. G.

Solubilities of symmetrical normal aliphatic secondary amines of high mol. wt.—See A., 1944, II, 248.

Influence of an adsorbed layer on cohesion and coalescence in liquids and in solids. C. Benedicks, and P. Sederholm (*Arkiv Mat. Ast. Fys.*, 1944, 30, A, 34 pp.).—Various experiments are described relating to the phenomenon of the floating drop, the stability of which is characterised by its time of existence (durability). This is ~ 10 sec. for EtOH. The phenomenon is largely due to absorption of moisture in the surface layers. It is shown by H_2SO_4 when this has an appreciable H_2O content. In a solution of saponin (which shows strong adsorption) the durability, and hence the adsorption, possesses a max. at a concn. of $\sim 1\%$. In malt beverages (possessing strong foaming and hence adsorption) the phenomenon is very prominent (durability 20—25 sec.). The presence of CO_2 in the liquid is necessary. When artificial adsorption layers are produced by thin oil films on H_2O the durability is very great. Fluid foams (containing only liquid matter) are studied, one of these being made from saponin solution and oil. Floating drops occur in molten paraffin, and there is a marked adsorption on solid paraffin. The cohesion between two plane surfaces was determined; this is high for freshly cut surfaces (adsorption excluded) but very low for cut surfaces after exposure to air. Similar results were obtained for solid Pb and Sn. L. S. G.

Cross-sectional areas of molecules adsorbed on solid surfaces. H. K. Livingston (*J. Amer. Chem. Soc.*, 1944, 66, 569—573).—Measurements have been made on the adsorption of N_2 , using the low-temp. method of Brunauer and Emmett (A., 1937, I, 510), and of H_2O , Pr^+OH and $n-C_4H_{10}$, by the sorption balance method, on graphite, quartz, anatase, and $BaSO_4$. Cross-sectional areas, calc. by the equations of Brunauer *et al.* (A., 1938, I, 190), are $H_2O = 10.6$, $Pr^+OH = 20.0$, $C_4H_{10} = 55.0$ sq. Å. per mol., relative to $N_2 = 15.4$ sq. Å., in agreement with vals. derived from density, X-ray and film-balance measurements. The val. for C_4H_{10} indicates that the mols. lie with long axes parallel to the solid surfaces. W. R. A.

Accommodation coefficient of helium on platinum. (Miss) P. Rolf (*Physical Rev.*, 1944, [ii], 64, 185—189).—Vals. obtained for a clean Pt surface at 77°, 193°, 273°, and 373° K. are 0.090, 0.043, 0.071, and 0.072 (± 0.004), respectively. For Pt in contact with He for 24 hr. or more, the respective vals. are 0.43, 0.071, 0.170, and 0.170. There is little absorption at 193° K., but strong van der Waals absorption appears at 77° K. and activated absorption at the higher temp. N. M. B.

Water sorption by starches.—See B., 1944, III, 132.

Simple, rapid method for determining maximal water-absorption of materials, especially applicable to small water-absorption values and very small samples. F. H. Müller (*Kolloid-Z.*, 1943, 105, 16—20).—Apparatus and procedure are described for determining manometrically the max. amount of H_2O taken up, e.g., by org. foils, on exposure to H_2O vapour. The method employs samples of 1—10 mg., is fairly rapid, and gives an accuracy of 10—15%, which is equally well attained for the lowest H_2O -absorption vals. R. H. F.

Photo-adsorption effects in the system pigment-fluid phase. J. A. Hedvall and S. Nord (*Arkiv Kemi, Min., Geol.*, 1943, 17, A, No. 11, 11 pp.).—The adsorption by red and black HgS of phenolphthalein from aq. EtOH solution and by CdS of α -naphtholphthalein from similar solutions has been investigated under varying light conditions. Light has little effect on adsorption by black HgS but red HgS adsorbs six times as much phthalein in light as in darkness. This difference is ascribed to the different electronic structures of red and black HgS. Black HgS and irradiated red HgS are conductors whereas in darkness red HgS is an insulator. Irradiated CdS adsorbs phthalein in darkness. In each case adsorption in darkness is increased by presence of excess of S in the sulphide. A parallel is drawn between these photo-adsorption effects and the Becquerel or photo-voltaic effect. C. R. H.

Dependence of absorptive property on the concentration of hydro-ions and of metallic cations. E. N. Gapon (*J. Gen. Chem. Russ.*, 1943, 13, 382—390).—The equation derived by Gapon, viz., $S = S_0 + \beta \log (\alpha_M^{1/2}/\alpha_H)$ (1) ($S = g$ -equiv. of metal cations absorbed per g. of absorbent, $\alpha_M =$ activity of metal ions and $\alpha_H =$ activity of H ions, $z =$ valency of cations, $\beta =$ const.) on theoretical grounds is compared with Gortikov's empirical equation $S = a + \beta pH - \gamma pM$ (2) (a , β , and γ being consts., $pM = \log [\text{metal ions}]^{-1}$) and is tested on the data of Ivanov obtained for the action of buffered solutions on black earth (chernozem). Equations (1) and (2) hold for Na^+ ($a = -2.2$, $\beta 6$), K^+ ($a = -3.3$, $\beta 6.4$), Mg^{++} ($a = -6.6$, $\beta 7.6$), and Ba^{++} ($a = -7.5$, $\beta 7.8$) but not for Ca^{++} , and an order of the standard absorbing capacity δ (g.-equiv. absorbed per 100 g. of absorbent at pH 7 and pM 0) is derived. For alkaline solutions an equation $S = a_0 \beta_0 \log a_+$, where a_+ is the mean activity of the alkali, holds in respect of Ivanov's data for Na ($\beta_0 12.0$), K^+ ($\beta_0 12.8$), Mg^{++} ($\beta_0 11.4$), and Ba^{++} ($\beta_0 11.7$) (cf. Nikolski, B., 1935, 71). F. H. I.

Activation of a palladium surface by the glow discharge.—See A., 1944, I, 162.

Mechanism of chemical reactions between solids.—See A., 1944, I, 180.

Ionic interaction in the double electrolytic layer. O. Essin and V. Schichov (*J. Phys. Chem. Russ.*, 1943, 17, 236—246).—The potential V of the electrocapillary max. is measured for Hg in 0.01—3N-KI, 0.01—10N-KCNS, 0.01—3N-NaBr, and 0.01—5N-NaCl. V increases with $\log C$ ($C =$ concn. of the salt) more steeply than linearly, although Stern's theory predicts an expression $V \propto \log C$. To account for this discrepancy it is assumed that ions in the double layer are either distributed at random or form rigid ion pairs oriented towards the interface, but neither of these assumptions appears satisfactory. The interaction between parallel ion dipoles in the interface is calc. on the pattern of crystal lattice calculations. J. J. B.

Osmosis. L. Plantefol (*Compt. rend.*, 1943, 217, 33—35).—A discussion of the phenomena of osmosis and osmotic pressure, as related to the characteristics of permeable and semipermeable membranes. The transfer of H_2O across a membrane depends, both as regards direction and magnitude, on the effect of the crystalloid on the membrane. The term osmosis should be applied to those cases where the controlling force is a process of hydration. P. G. M.

Causes of the dichroism of colloidal metals. P. A. Thiessen (*Z. anorg. Chem.*, 1943, 250, 352—356).—The dichroism of colloidal metals in stretched gelatin is sometimes due to the orientation of rod- or leaf-shaped particles of metal, but in other instances to the orientation of non-metallic crystals in which spherical particles of metal are embedded. F. J. G.

Disperse structure of solid systems and its thermodynamic basis. XV. D. Balarew (*Kolloid-Z.*, 1943, 105, 26—29).—The effect of the structure of the Ag cathode on the decomp. potential of Ag ions in $AgNO_3$ solution, and the effect of heating on the catalytic activity of powdered Ag, on the hardness of Au, and on the electrical conductivity and strength of Cr-Ni wires are considered in relation to the intermixing of surface components of the solid metals. R. H. F.

Thixotropy of montmorillonite. H. G. F. Winkler (*Kolloid-Z.*, 1943, 105, 29—38).—The degree of thixotropy is expressed quantitatively by the "thixotropic limit," which is the vol. of liquid required per vol. of solid to give a system of setting time 1 min. under specified conditions. The increase in thixotropy with temp. follows the Arrhenius equation. Montmorillonite (I) differs fundamentally from other minerals, e.g., kaolinite, in its thixotropic behaviour, as shown by the diminished thixotropy in presence of electrolytes and the lower thixotropy obtained with org. liquids as compared with H_2O . The differences are due to penetration by H_2O into the layers in the crystal aggregate, causing internal swelling. If the swelling- H_2O is replaced in the crystals by other liquids, e.g., EtOH, the thixotropic behaviour is altered. There is also a pronounced difference between fully swollen and unswollen (I). Progressive reduction of particle size, by subjecting suspensions of (I) to ultrasonic waves, results in increased thixotropy. The energy necessary to liquefy systems of different concns. is examined. R. H. F.

Fibre structure in dispersions of soap in mineral oil. W. Gallay, I. E. Puddington, and J. S. Tapp (*Canad. J. Res.*, 1944, 22, B, 66—75).—By microscopic examination of Et_2O -extracted greases (soaps dispersed in mineral oil) using polarised light, reliable determinations of the fibre length of metallic soap constituents can be made. Ca and Al soaps give fibres which are generally too small to be measured by this method and the resulting grease has a smooth texture. Na soaps give a wide range of fibre lengths which result in greases with characteristics ranging from very smooth to very ropy. The large fibres are made up of smaller units more or less parallelised. This orientation to larger units is easily brought about by applying a directional force, especially in presence of glycerol (I). In absence of (I) the soap is not wetted by the mineral oil, and on cooling a mixture of soap and oil very short fibres are obtained. In the recrystallisation

of soap in the commercial manufacture of grease, the growth of the crystallites first formed is aided by (I), which exerts a solvent action on the soap and enables the oil to wet the crystallites which, as a result of collisions, form larger crystallites or fine fibres. Formation of larger fibres then follows as a result of directional forces set up by agitation during cooling. C. R. H.

Recrystallisation of sodium soaps in mineral oils. W. Gally and I. E. Puddington (*Canad. J. Res.*, 1944, 22, B, 90—102).—The effect of various factors on the recrystallisation of Na soaps in mineral oils has been examined. In absence of any shearing stress, set up, e.g., by agitation, slow cooling favours recrystallisation, and the presence of free acid causes the soap to recrystallise in the form of fibres. Large fibres are also formed in presence of polar substances such as H_2O or glycerol, or if the oil itself is of a polar nature. The application of shearing stresses favours fibre formation. Recrystallisation from a non-polar oil must be regarded as recrystallisation from a hot melt. The presence of polar substances causes the oil to exert a solvent action on the soap; recrystallisation is then partly of the hot melt and partly of the solvent type. In such cases shearing forces play a large part in orientation of the soap micelles. C. R. H.

Effect of high shearing stresses on recrystallisation of sodium soaps in mineral oils. W. Gally and I. E. Puddington (*Canad. J. Res.*, 1944, 22, B, 103—108).—High shearing stresses bring about recrystallisation of Na soaps at temp. < the plasticity point of the soap. The length of soap fibre increases with increase in the polarity of the oil, with decrease in the η of the oil, and with increase in the degree of unsaturation of the soap. Neither variation in free acidity or alkalinity nor addition of glycerol has any appreciable effect on the length of the fibres formed. Discussion of the action of shearing stresses leads to the view that long soap crystals are produced by a shearing of the double soap mols. on slip planes between melted hydrocarbon chains, recrystallisation being thus induced on molten portions of the soap. C. R. H.

Low-temperature saponification of anhydrous systems. W. Gally and I. E. Puddington (*Canad. J. Res.*, 1944, 22, B, 76—89).—At 50—60° finely divided NaOH and $Ca(OH)_2$ rapidly saponify fatty acids dissolved in mineral oil. The physical properties of the soap dispersions depend on the degree of unsaturation of the fatty acid. Dispersions of high η are obtained with saturated acids. As the result of an agglomeration effect which lowers dispersion, unsaturated acids give products of low η . The saponification of fats is more difficult, only mutton tallow being saponified rapidly. Al, Mg, Ba, Pb, Li, Ni, Co, and Mn soaps have been similarly prepared and the physical properties of some of them are described. C. R. H.

Peptisation of humic substances by alkaline solutions. A. Boutsier (*Compt. rend.*, 1943, 217, 46—48).—Solutions of alkalis dissolve humic acids from lignite, and, on addition of acids, the humates are decomposed giving colloidal solutions of humic acids. Dil. NaOH is more effective than conc. in dissolving humic acids. The dissolution has been studied with NaOH and aq. NH_3 in the hot (in N_2) and in the cold. The most effective concn. of NaOH is 3%. If carried out in air, the more conc. NaOH dissolves more humic acid in the hot than dil. NaOH, but this is due to the effect of atm. O_2 . In the cold, this effect is negligible. A. J. M.

Relationship between solution viscosity and mol. wt. in the amylose series. J. F. Foster and R. M. Hixon (*J. Amer. Chem. Soc.*, 1944, 66, 557—560; cf. A., 1943, II, 221).—Osmotic pressure and η_{sp} of $CHCl_3$ solutions of maize- (I), tapioca- (II), and potato- (η_{sp} only)-amylose acetates have been determined. Mol. wts. of (I) and (II) are 42 and 75×10^3 . The exponent, α , in the relation $\eta_{sp} = KM^\alpha$ (M = mol. wt., K a const.) has a val. > 1, as expected from the high rigidity of the Fischer-Hirschfelder models of amylose. The rigidity of amylose acetates in $CHCl_3$ is the same as that of amyloses in $(CH_3NH_2)_2$. W. R. A.

Theory of solutions of high-polymeric substances. A. Munster (*Kolloid-Z.*, 1943, 105, 1—9).—The methods of statistical mechanics are used to explore the theoretical behaviour of solutions of high polymers. The laws of ideal solutions are not valid when solvent and solute mols. are of widely different sizes; the problem is treated by subdividing the high-polymer mol. into units comparable in size with solvent mols. A coherence condition is introduced because a certain group of units always forms one large mol. The significant factor is the no. of possible arrangements of the polymer mols., and a formula is derived for the thermodynamic potential of the dil. solution, introducing a "virtual molar fraction." This leads to modified formulæ for chemical potential, lowering of v.p., and osmotic pressure, which become identical at infinite dilution with the formulæ for ideal solutions. A consequence of solvation is that not all configurations have the same energy, and an additional term is required in the expression for the thermodynamic potential of the solution. R. H. F.

Mol. wt. and mol. wt. distribution in high polymers. General introduction. H. W. Melville (*Trans. Faraday Soc.*, 1944, 40, 217—220).—A short survey of problems and methods of investigation. F. L. U.

Mol. wt. and shape of macromolecules in solution. H. Campbell and P. Johnson (*Trans. Faraday Soc.*, 1944, 40, 221—233).—Measurements of viscosity, sedimentation rate, and diffusion const. for globular proteins (egg- and serum-albumins, ground-nut globulin) and cellulose nitrate (N 12.2%) (I) are reported and discussed from the point of view of mol. wt. and shape. Mol. wts. of (I) fractions are calc. by the use of various equations relating η to mol. shape. The validity of the equations remains in doubt until accurate vals. for the mol. wt. of (I) fractions have been established by independent methods. Experimental conditions needed for accurate work on sedimentation and diffusion are discussed, and the importance of using solutions of suitably high dilution is emphasised. Data so far obtained indicate that (I) mols. in $COMe_2$ are fully extended but slightly flexible, with a diameter increased by solvation to ~ 17.6 Å. F. L. U.

Osmotic pressure of high polymer solutions and mol. wt. E. A. W. Hoff (*Trans. Faraday Soc.*, 1944, 40, 233—236).—Osmotic pressures of $CHCl_3$ solutions of cellulose acetate (I) and polymethyl methacrylate have been measured with an osmometer as described by Carter and Record (A., 1939, I, 318). The Cellophane membranes used became less permeable after prolonged contact with the solutions, and this behaviour led to difficulties when working with solutes having a wide range of particle size. Plots of Π/c against c (Π = osmotic pressure, c = concn.) were never rectilinear, those of Π/c against Π only for some specimens of (I). Where both plots are curved it is advantageous to draw them on the same diagram and extrapolate both to meet at $c = 0$. F. L. U.

Mol. wt. of rubber and related materials. V. Interpretation of mol. wt. measurements on high polymers. G. Gee (*Trans. Faraday Soc.*, 1944, 40, 261—266).—Osmotic and viscosimetric methods of ascertaining the mol. wt. of polymers are discussed. F. L. U.

Theory of viscosity of solutions of macromolecular substances. I. General considerations. P. H. Hermans, J. J. Hermans, and D. Vermaas (*Kolloid-Z.*, 1943, 105, 199—204).—General views on the η of solutions of macromol. substances are put forward. The theories of η of very dil. solutions are discussed. These theories have assumed the presence of either rigid anisodiametric particles or rigid knots of mols. It is, however, very probable that such knots will be deformed and broken down into their original state by the process of streaming. The investigation of the deformation forces and the relaxation time of the deformation gives quant. agreement with experiment. Amongst the interactions between the solute mols. the association linkings between the chains must play an important part. These associations take place at local points of attraction and are of limited life. They influence η considerably. The above general considerations apply also to the formation and structure of gels. A. J. M.

Structure mechanics of viscous elastic continua. IX. Hysteresis in rheonomic systems. H. Umstätter (*Kolloid-Z.*, 1943, 105, 182—190).—In medium ranges of tangential pressure flow curve measurements are less reproducible than in the higher or lower ranges. This is due to a hysteresis effect. Space diagrams for the Maxwell equation are drawn for various conditions of force and velocity. The hysteresis is thus shown to be characterised by thixotropy (analogous to retentivity) and elasticity of flow (analogous to coercivity), but complete analogy with the magnetic case can be obtained only for solids. The structure-mechanical properties of substances can be expressed in terms of three fundamental consts.—shear elasticity, relaxation time, and the limiting val. of the film thickness. A. J. M.

Cataphoresis of purified fractionated kaolin particles.—See B., 1944, I, 267.

Boundary anomalies and electrophoretic analysis of colloidal mixtures. H. Svensson (*Arkiv Kemi, Min., Geol.*, 1943, 17, A, No. 14, 15 pp.).—A mathematical theory of boundary anomalies in colloidal mixtures has been developed and tested qualitatively by means of a series of electrophoresis experiments with hog serum, in which a successive decrease of boundary anomalies was obtained by using phosphate buffers containing increasing concns. of NaCl. The apparent albumin content decreases with increasing [NaCl], and high [NaCl] is necessary to obtain vals. approaching the limiting val. The albumin content of hog serum approaches 42% at infinite [NaCl]. The necessity of eliminating boundary anomalies when determining albumin concns. in serum is emphasised. C. R. H.

VI.—KINETIC THEORY. THERMODYNAMICS.

Dissociation constants and pH titration curves at constant ionic strength from electrometric titrations in cells without liquid junction. Titrations of formic acid and acetic acid. R. G. Bates, G. L. Siegel, and S. F. Acres (*J. Res. Nat. Bur. Stand.*, 1943, 30, 347—359).—pH titration curves for HCO_2H and $AcOH$ in the cell $Pt|H_2|H^+, Cl^-||AgCl|Ag$ at const. $[Cl^-]$ and const. μ are recorded. The pK vals. are: HCO_2H , 3.742; $AcOH$, 4.754. F. J. G.

Second ionisation constant of deuterocarbonic acid. J. Curry and Z. Z. Hugus, jun. (*J. Amer. Chem. Soc.*, 1944, 66, 663—666).—The

e.m.f. of the cells $H_2|KHCO_3, K_2CO_3|KCl|AgCl, Ag$ in H_2O and $D_2O|KDClO_3, K_2CO_3|KCl|AgCl, Ag$ in 98.9% D_2O has been measured. Using MacInnes and Belcher's val. of 5.61×10^{-11} (A., 1933, 904) for the ionisation const. of HCO_3^- , the ionisation const. of DCO_3^- has been calc. as 1.42×10^{-11} . W. R. A.

Hydration of ions. J. Swygndcauw (*J. Phys. Radium*, 1942, [viii], 3, 117—120).—The action of $CO(NH_2)_2$, glucose, and sucrose is similar to that of gelatin in solutions of a salt; they undergo hydration, and thereby reduce the hydration of the ions of the salt. N. M. B.

Ionic strength valency of ferrohaemoglobin. R. D. Bernard (*J. Biol. Chem.*, 1944, 153, 91—111).—When solutions of ferrohaemoglobin (I) containing NaCl or NaBr are titrated with NaOH the change from (I) to globin ferrohaemochromogen takes place at a slightly lower pH than in salt-free solutions. Each salt exerts an effect on both the acid- and base-combining powers of (I) everywhere on the titration curve except at the isoelectric point, thus increasing the buffer power of (I). The ionic strength valency of (I) rises from 0 (at the isoelectric point) to a max. of ~ 3 on the basic side of the titration curve. Substitution of $Ca(OH)_2$ for NaOH does not change the shapes of the titration curves, but more Ca than Na eqvls. are bound by (I) at pH vals. $>$ the isoelectric point. Measurement of the effect of (I) on the distributed capacity of the inductive component of an antiresonant electrical circuit suggests that (I) is without effect on the dielectric const. of NaCl solutions for frequencies 12—45 megacycles per sec. Theoretical considerations support this. The magnitude of the difference between Na^+ and Ca^{++} is $>$ can be explained by the Debye-Hückel theory. Possible causes for this are a sp. ion effect or a smaller degree of dissociation for Ca than for Na ferrohaemoglobinate. C. R. H.

System bromine-boron bromide. J. Cueilleron (*Compt. rend.*, 1943, 217, 112—113).—The system has been examined by the cryoscopic method. BBr_3 is the only compound of B and Br existing under the temp. conditions used (-8.8° to -60°). Br and BBr_3 form a eutectic containing 80% of BBr_3 , m.p. -60.4° . A. J. M.

Azeotrope in the system *n*-butane-methyl bromide. J. D. Holdman (*J. Amer. Chem. Soc.*, 1944, 66, 661).—An azeotrope, b.p. -4.4° , containing 58.1 ± 0.5 mol.-% of $n-C_4H_{10}$, has been observed in the $n-C_4H_{10}$ -MeBr system. W. R. A.

Equilibria in reduction of chromic oxide by carbon.—See B., 1944, I, 275.

System $CaO-Al_2O_3-H_2O$ at 21° and 90° . L. S. Wells, W. F. Clarke, and H. F. McMurdie (*J. Res. Nat. Bur. Stand.*, 1943, 30, 367—409).—Equilibrium studies on the system $CaO-Al_2O_3-H_2O$ at 21° and 90° are recorded. The so-called hexagonal Ca_3 aluminate hydrate consists of $2CaO, Al_2O_3, 8H_2O$ (I) and $4CaO, Al_2O_3, 13H_2O$ (II) intercryst. in equimol. proportions. On keeping in contact with solution, (I) affords (II) and $Al(OH)_3$. Both (I) and (II) are metastable with respect to the isometric $3CaO, Al_2O_3, 6H_2O$ (III). Diagrams are given showing the solubility relationships of (I), (II), and (III). The only stable solid phases are (III), $Ca(OH)_2$, and gibbsite, $Al_2O_3, 3H_2O$. F. J. G.

Heats of formation of beryllium, magnesium, and calcium sulphides. H. von Wartenberg (*Z. anorg. Chem.*, 1943, 252, 136—143).—By comparison of the heats of dissolution of the metals and the sulphides the heats of formation of BeS, MgS and CaS have been determined as 56.1 ± 1 , 83.9 ± 0.5 , and 114.3 ± 0.5 kg.-cal. per g.-mol. F. J. G.

VII.—ELECTROCHEMISTRY.

Oxidation-reduction potentials: their significance and applications. H. I. Stonehill (*J. Soc. Dyers and Col.*, 1944, 60, 176—183).—A review. C. S. W.

Electrode polarisation in electrodeposition of silver from complex electrolytes. A. Levin (*J. Phys. Chem. Russ.*, 1943, 17, 247—257).—Potential-c.d. curves are determined for Ag and dropping Hg cathodes in some $[Ag(NH_3)_2]_2SO_4$, three $K_2[Ag(CNS)_4]$, and three $K_3[AgI_4]$ solutions. The polarisation E is reduced by stirring, and $E - \text{const.}$ $0.058 \log(1 - D/D_0)$ for both stirred and resting solutions; D is the c.d. corresponding to E , and D_0 is the limiting c.d. for the given intensity of stirring; D_0 is defined by the condition that at $D > D_0$, E increases with D very rapidly. The validity of the equation and the influence of stirring show that the polarisation is a pure concn. polarisation. The behaviour of the anodic polarisation on Ag anodes is similar. J. J. B.

VIII.—REACTIONS.

Kinetics of complex homogeneous reactions. I. General theory of complex reactions. N. N. Semenov (*J. Phys. Chem. Russ.*, 1943, 17, 187—214).—The types of homogeneous reactions taking place in several steps are systematically reviewed, the main types being linear sequence of reactions, unbranched chain reaction, and branched chain reaction. General rules for branched chain

reactions are given, and Bodenstein's method of stationary concns. of intermediate compounds is extended for non-stationary reactions. J. J. B.

Polymeric phosphates. IV. Rate of hydrolysis of pyrophosphate, tripolyphosphate, and hexametaphosphate. R. Watzel (*Chemie*, 1942, 55, 356—359).—The hydrolysis of $Na_4P_2O_7$ (I), $Na_6P_3O_{10}$ (II), and $(NaPO_3)_x$ (III) has been studied in 1% solution at 60° and 100° and pH (controlled) 0.6—13.0; results were confirmed by examination of the Ca-sequestering power of the hydrolysates. The rate of hydrolysis of (I), (II), and (III) is high at low pH, and falls rapidly with increasing pH; at pH 7 (II) and (III) are only slowly, but (I) is still quite rapidly, hydrolysed. Above pH 7, the rate of hydrolysis of (I) falls rapidly until pH 10, when it is stable indefinitely, of (II) falls slowly with increase of pH to 13, and of (III) falls to a min. at pH 8—9 and then rises again slowly (all at 100°). The rate of hydrolysis is in all cases greatly reduced at 60° and the compounds can be treated as stable indefinitely above pH 7. In the range 0.1—1.0% the rate of hydrolysis of the compounds increases with increasing concn. at pH 7—10, and, with (III) only, with decreasing concn. at pH 3 and 13, but the effect is small compared with those of pH and temp. M. H. M. A.

Non-stoichiometric equations. (A) Ö. F. Steinbach. (B) W. T. Hall. (c) A. Lehrman (*J. Chem. Educ.*, 1944, 21, 66—69, 201—202, 202—203).—Crit. discussions. L. S. T.

Flame spectrum of carbon monoxide. III. The cool flame.—See A., 1944, I, 190.

Homogeneous thermal decomposition of cyclopentane. L. Küchler (*Z. physikal. Chem.*, 1943, B, 53, 307—319).—The decomp. velocity was measured at 500 — 600° by a static method, and the products were separated by desorption. The decomp. is about half a dehydrogenation to cyclopentadiene and half a ring cleavage in which C_2H_4 and C_2H_2 are formed. Small quantities of CH_4 are also produced. The dehydrogenation occurs in two stages via cyclopentene; the first stage is rate-determining; it is of the first order and has an activation energy of ~ 75 kg.-cal. per g.-mol. The ring cleavage is autocatalytic, the acceleration being caused by the C_2H_4 and C_2H_2 produced. It is improbable that chain reactions play any part in the process. J. F. H.

Thermal decomposition of acetaldehyde. J. C. Morris (*J. Amer. Chem. Soc.*, 1944, 66, 584—589).—The products of the thermal decomp. of $MeCHO$ (I) and CD_3CDO (II) and their mixtures at 500° have been studied by means of their infra-red absorption spectra. Abs. reaction rates have been determined. CH_4 , CD_4 , MeD , and CHD_3 are the only methane-species produced in any quantity, indicating that decomp. is truly unimol., and that chain reactions play but a minor part, being probably induced by impurities. Abs. reaction rates only half as large as previous determinations support this view. The rate of decomp. of (I) is 1.3—1.4 times that of (II). W. R. A.

β -Lactones and β -lactonic acids. IV. Rate of fission of the β -lactone ring. M. M. Schemjakin and N. S. Vulfson (*J. Gen. Chem. Russ.*, 1943, 13, 448—456).— β -Lactones of isopropylidene- (I) and benzylidene-malonic acid (II) were treated with 0.1N. aq. NaOH at various temp. The unimol. reaction coeffs. were, (I): $6.4091 \times 10^{-3}/75^\circ$, 7.5275×10^{-3} (temp. ?), and 7.105×10^{-3} (temp. ?); 1.6196×10^{-3} and $1.6949 \times 10^{-3}/85.5^\circ$; 6.0977×10^{-3} , 6.5235×10^{-3} , $6.25473 \times 10^{-3}/104^\circ$; (II): 8.5548×10^{-3} , 7.9102×10^{-3} , $8.0789 \times 10^{-3}/76^\circ$; 2.127×10^{-3} , $2.282 \times 10^{-3}/85^\circ$, 1.018×10^{-3} , $9.9 \times 10^{-3}/103^\circ$, whence the calc. heat of activation of scission of the ring of (I) is 19,323 g.-cal., and of the ring of (II) is 22,832 g.-cal. F. H.

Interpretations of reactions in the carbohydrate field in terms of consecutive electron displacement.—See A., 1944, II, 250.

[Slow] oxidation of ketones and aromatics in the gaseous phase.—See B., 1944, II, 193.

Autoxidation of β -elaeostearic acid. Application of the spectrophotometer to the study of the course and the kinetics of the reaction. R. W. Brauer and L. T. Steadman (*J. Amer. Chem. Soc.*, 1944, 66, 563—569).—The oxidation of $n-C_{17}H_{33}OAc$ solutions of β -elaeostearic acid (I) by mol. O_2 has been studied at 64.5° by the simultaneous determination of O_2 uptake and absorption spectra. Plots of O_2 uptake rates against initial concn., at various stages in the reaction, are linear above 0.05 g. per c.c., but deviate from linearity below this concn. During the oxidation, the intensity of the absorption band of (I) at 2685 Å. decreases, and that of a new band at <2500 Å. first increases and finally decreases. The rate of decomp. of the triene group of (I) has been calc. from the O_2 uptake curves and from the relation between absorbed O_2 and residual triene groups. Initially, decomp. of (I) needs mol. of O_2 , suggesting that the initial reaction results in a dimerisation of (I) involving C—C bonds, and that the peroxides formed during the reaction induce a parasitic polymerisation. Dimerides have been isolated from the reaction mixture. O_2 uptake can be approx. calc. for the early stages from the absorption spectra, if it be assumed that two mols. of (I) react with one mol. of O_2 to give a dimeric diene, which further reacts with one mol. of O_2 giving spectrographically inert products capable of

absorbing two mols. of O_2 per mol. of (I) originally present. The rate of O_2 absorption becomes small after the absorption of two mols. per mol. of (I). The two mols. of O_2 may be recovered as a dibasic acid, probably a polymeride of (I), which loses $\frac{1}{2}$ of the absorbed O_2 on boiling with 2% aq. KOH. W. R. A.

Catalytic studies on alloys. XI. Copper-palladium and copper-platinum alloys as catalysts for the hydrogenation of ethylene. G. Rienacker, E. Müller, and R. Burmann (*Z. anorg. Chem.*, 1943, 251, 55—70).—The behaviour of Cu-Pd and Cu-Pt mixed crystals as catalysts for the hydrogenation of C_2H_4 has been studied. Alloys with ≤ 47 at.-% Pd and ≤ 16 at.-% Pt are comparable in efficiency with pure Pd and Pt, although the activation energies decrease steadily from pure Cu to pure Pd or Pt. Alloys with ordered structure show activation energies $<$ those for the corresponding alloys with disordered structure. F. J. G.

Generalised acid-base catalysis. I. Condensation of *o*-benzoylbenzoic acid in sulphuric acid. W. F. Luder and S. Zuffanti (*J. Amer. Chem. Soc.*, 1944, 66, 524—526).—The condensation of *o*- $C_6H_4BzCO_2H$ to anthraquinone (I), catalysed by oleum, is discussed with respect to the generalised theory of acid-base catalysis. The postulate of a cyclic ion does not impair the applicability of the latter. Inhibition of the reaction by (I), $AlCl_3$, HCl , $CuCl_2$, and HF is ascribed to a reduction in the acid strength of the oleum. W. R. A.

Promoting effect of some metal oxides on iron-copper contacts used in synthesis of gasoline from water-gas.—See B., 1944, I, 258.

Sodium peroxide bleaching of mechanical pulps. Control of metal catalysts in the bleaching operation.—See B., 1944, II, 228.

Mechanism of electrolysis. R. Audubert (*J. Phys. Radium*, 1942, [viii], 3, 81—89).—By taking into account the activation energy of the ions and the ionisation of the discharge products, a relation is obtained representing the intensity variation as a function of potential. Results are verified by tabulated and graphical experimental data. From the theory developed, activation energies of different processes and the mechanism of discharge are deduced. N. M. B.

Plating magnesium [with nickel and silver].—See B., 1944, I, 281.

Recent developments in zinc plating.—See B., 1944, I, 281.

Cadmium plating.—See B., 1944, I, 281.

Impurities in cobalt electrowinning.—See B., 1944, I, 281.

Electrochemical mechanism of corrosion. G. Masing (*Z. anorg. Chem.*, 1943, 252, 164—169).—Contrary to the observations of Todt (A., 1929, 145, 270) the corrosion of both Cd and Fe when in contact with Cu or Pt in an AcOH buffer with the H_2O -line covered \propto the sum of the surfaces of the two metals. F. J. G.

Electrolytic reduction of acetophenone in alkaline solution.—See A., 1944, II, 218.

Photo-reduction of ferric chloride in presence of aqueous acetone and anhydrous ether. M. Prasad and P. R. Bavdekar (*Proc. Indian Acad. Sci.*, 1943, 18, A, 373—382).—The photo-reduction of $FeCl_3$ by radiation of mean λ 4725, 5975, and 6625 Å. in aq. $COMe_2$ and anhyd. Et_2O has been investigated. The reductions are unimol., with velocity coeffs. markedly affected by changes of temp. and λ , and rates \propto incident intensity. Quantum yields increase with decreasing $[FeCl_3]$, and with increasing temp. and ν of the exciting radiation, and are ~ 0.5 for aq. $COMe_2$ and ~ 1.0 for anhyd. Et_2O . W. R. A.

Reactions shown by spectra of electron affinity of chromous and ferrous ions. B. J. Dain, B. F. Kutza, and E. A. Liberzon (*J. Phys. Chem. Russ.*, 1943, 17, 226—235).—The absorption in ultra-violet of $CrSO_4$ solutions was determined between 0.02 and 0.55 μ ; the Lambert-Beer law was valid at < 0.09 mol. per l. The long-wave frontier was at ~ 3500 Å., i.e., at 3.5 e.v., in agreement with the work of removing an electron from aq. Cr^{++} . Solutions of $FeSO_4$ and $CrSO_4$ evolve H_2 when illuminated with $\lambda < 3000$ Å.; the rate (v_1 for Fe^{++} and v_2 for Cr^{++}) of evolution is independent of temp. (17—50°). H_2SO_4 accelerates the rate: v_1 is raised 4.4 times when $[H_2SO_4]$ increases 120 times, and v_2 rises 1.8 times when $[H_2SO_4]$ increases 40 times; this acceleration is so small that OH^+ cannot be formed in the primary reaction, which is more likely to result in formation of an intermediate compound of Fe^{+++} (or Cr^{+++}) with negatively charged H_2O . v_1 is lowered by Fe^{+++} and becomes immeasurably small when $[Fe^{++}] : [Fe^{+++}] = 20 : 1$. v_2 is not affected by Cr^{+++} , which obviously is not reduced by at. H. The quantum yield for Fe^{++} is 0.1—0.2 and that for Cr^{++} is ~ 0.4 , of that for CH_2Cl-CO_2H . J. J. B.

Photochemical after-effect: decomposition of hydrogen peroxide by potassium ferricyanide. B. B. Lal and C. P. Singhal (*Current Sci.*, 1944, 13, 78—79).—A large after-effect was observed in decomp. by pre-insolated $K_3Fe(CN)_6$, especially when some unilluminated $K_3Fe(CN)_6$ is also present in the reaction mixtures. The irradiated salt solution shows a much enhanced reactivity towards H_2O_2 in the dark, and this enhanced effect which shows itself as a photochemical after-effect is retained for a long time, but diminishes gradually on keeping in the dark. Tabulated data are reported, the mechanism

of reaction is discussed, and evidence of the formation of $K_2Fe(CN)_6 \cdot H_2O$ by irradiation of $K_3Fe(CN)_6$ is given. N. M. B.

Reactions of hydrocarbons with sulphuryl chloride and with sulphur dioxide-chlorine mixtures. H. J. Schumacher and J. Stauff (*Chemie*, 1942, 55, 341—345).—Chlorination of hydrocarbons by SO_2Cl_2 (I) in light or in presence of Bz_2O_2 (II) always gives some $R \cdot SO_2Cl$, the yield falling as the temp. rises owing to decomp. of $R \cdot SO_2Cl$ and increase in the rate of chlorination [*cyclohexane* in light at 30° gives 70% of $C_6H_{11} \cdot SO_2Cl$ (III) at 70° 20%], but $R \cdot SO_2Cl$ must be determined by hydrolysis of the reaction product and not by distillation, when decomp. occurs, catalysed by (II) [the rate of decomp. of (III) at 100° is increased 10-fold by 2% of (II)]; hence Kharasch's failure to detect $R \cdot SO_2Cl$ (A., 1939, II, 497; 1940, II, 3, 72, 172, 202, 363). Chlorination by (I) in presence of (II) occurs, as in light, via Cl_2 , the dissociation of (I) being amply fast, and the mechanism put forward by Kharasch (*loc. cit.*) is unnecessary. The photochemical chlorination is catalysed by active C owing to its catalysis of the dissociation of (I), but the reaction in presence of (II) is inhibited, as it also catalyses the decomp. of (II). The slow chlorination of, e.g., $CHCl_3$ or $(CHCl_3)_n$ in presence of (II) is due to their reaction with (II), causing chain-breaking. C_2H_5N has no catalytic effect on the production of $R \cdot SO_2Cl$ from RH and SO_2Cl_2 , acting only by removing SO_2 stoichiometrically and thus causing a high initial $[Cl_2]$ which shortens any induction period due to the presence of chain-breakers (usually dissolved O_2); with pure reagents there is no induction period and C_6H_5N has no effect. Illumination is preferred to the presence of (II), as the decomp. of (II) is very slow at the temp. (30—50°) necessary to minimise decomp. of $R \cdot SO_2Cl$, but replacement of (II) by a less stable peroxide gives satisfactorily rapid reaction. In the photochemical reaction: $SO_2 + Cl_2 \rightarrow (I)$, $k \propto I \times [SO_2]^{0.5-1.0}$, and is independent of $[Cl_2]$, $[O_2]$, and p ; the quantum yield is < 1 . There is no evidence of $\cdot SO_2Cl$ formation. The homogeneous thermal decomp. of (I) is immeasurably slow at 100°, but moderately rapid when sensitised by illuminated Cl_2 . The kinetics of the photochemical reaction: $n \cdot C_7H_{15} + SO_2 \rightarrow n \cdot C_7H_{15} \cdot SO_2Cl$ (IV) + HCl , have been studied at 25° in CCl_4 , using light of $\lambda = 436 m\mu$, by photoelectric determination of $[Cl_2]$. $-d[Cl_2]/dt = 4.9 \times 10^{-2} \times [(IV)] \times I^{0.6}$, and is independent of $[SO_2]$ above a min. concn.; the apparent activation energy is ~ 6 kg.-cal., and the quantum yield $\sim 3.5 \times 10^4$. The following mechanism is proposed: $Cl_2 + h\nu \rightarrow 2Cl$; (IV) + $Cl \rightarrow C_7H_{15} + HCl$; $C_7H_{15} + SO_2 \rightarrow C_7H_{15} \cdot SO_2$; $C_7H_{15} \cdot SO_2 + Cl_2 \rightarrow (V) + Cl$. The chain is broken by: $2Cl \rightarrow Cl_2$. The reaction is inhibited by O_2 , the chain being broken by its reaction with C_7H_{15} ; this reaction is $< 10^4$ times as fast as the reaction of C_7H_{15} with SO_2 , which again is much faster than: $C_7H_{15} + Cl_2 \rightarrow C_7H_{15}Cl + Cl$. M. H. M. A.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Double compounds of sodium oxide and the bivalent oxides of the manganese elements. G. Woltersdorf (*Z. anorg. Chem.*, 1943, 252, 126—135).— ZnO , CuO , NiO , and CoO react with Na_2O at $\sim 450^\circ$ affording the compounds Na_2ZnO_4 ; Na_2ZnO_2 ; Na_4CuO_5 ; Na_4CuO_2 ; Na_4NiO_5 ; Na_4CoO_5 . F. J. G.

Production of sodium silicofluoride.—See B., 1944, I, 263.

Growth of crystals of potassium sodium tartrate. L. C. Baker (*New Zealand J. Sci. Tech.*, 1943, 25, B, 62—64).—Details of a method for growing crystals weighing 150—200 g. by seeding solutions saturated between 30° and 40° and cooling the solutions by lowering the temp. of a small insulated room are given. The cooling of solutions saturated at temp. $> 40^\circ$ yields a mixture of Na K tartrate and Na tartrate. Crystals were also grown between glass plates to restrict growth to the Y and Z axes. L. S. T.

Identification of the products of corrosion of lead by water in the presence of air, by means of their X-ray spectra. M. F. Taboury and E. Gray (*Compt. rend.*, 1943, 217, 211—213).—Two phases are present in the deposit formed on Pb when exposed to the action of H_2O in presence of air. One is cerussite, $PbCO_3$ (I), the other is hydrocerussite, $2PbCO_3 \cdot PbO \cdot H_2O$, identical with the product obtained by boiling a suspension of (I). The red powder occasionally formed on Pb near the surface of the H_2O has the spectrum of minium. A. J. M.

Chromamines. III. Preparation of diacidodiethylenediamino-salts by thermal decomposition of triethylenediamine luteo-salts. C. L. Rollinson and J. C. Bailar, jun. (*J. Amer. Chem. Soc.*, 1944, 66, 641—644).—The thermal decomp. of $[Cr en_3]Cl_3 \cdot 3.5H_2O$ (I) at 100° and of $[Cr en_2]CNS_2 \cdot H_2O$ (II) at 130° has been investigated. NH_4Cl and NH_4CNS catalyse conversion of (I) into *cis*- $[Cr en_2Cl_2]Cl$ (III) and of (II) into *trans*- $[Cr en_2(CNS)_2]CNS$ (IV). The prep. of the monohydrates of (III) and (IV) by this method, giving 50 and 60% yields, are described. W. R. A.

X-Ray examination of patches of oxide formed on iron at high temperatures. J. Bénard (*Compt. rend.*, 1943, 217, 77—78).—If Fe is heated in air to 900° it becomes covered with a layer of oxide, chiefly FeO . If this patch is removed, and again heated to 900°,

it rapidly becomes Fe_2O_3 . It is supposed that there is a diffusion of Fe towards the oxide during the process of oxidation. This has been verified by X-ray determinations, the parameters of FeO being found at various temp. Fe can dissolve in FeO, causing an increase in a from 4.282 Å. to 4.300 Å. at 900°. FeO nearer the Fe surface has a larger a , indicating that FeO in the neighbourhood of the metal surface is saturated with Fe. Similar results are obtained at lower temp., a being always ~ 4.300 Å., but at the surface exposed to the atm. a is not as low as 4.282 Å. A. J. M.

Reducibility of oxides and sulphides in metallurgical processes.—See B., 1944, I, 272.

X.—LECTURE EXPERIMENTS AND HISTORICAL.

Experiment in colorimetry and reaction kinetics for physical chemistry. R. Wistar and L. Nelson (*J. Chem. Educ.*, 1944, 21, 94—95).—The coupling of diazotised sulphanilic acid with 1:4- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ acid to form an amber-coloured solution is followed colorimetrically to 77% completion in ~ 20 min. at 20°. Procedure is detailed. L. S. T.

[Laboratory] preparation of magnesium nitride. F. Fromm and P. J. Rivera (*J. Chem. Educ.*, 1944, 21, 196).—Well-dried N_2 from NH_4NO_3 is passed for several hr. over Mg powder contained in a porcelain boat and heated between 300° and 700° in a hard-glass tube. Traces of H_2O produce MgO . L. S. T.

Removal of electrolytes from solutions by ion exchange. Lecture demonstration experiment. F. C. Nachod and S. Sussman (*J. Chem. Educ.*, 1944, 21, 56—58).—Removal of salts from tap- H_2O , of sucrose from H_2O , and of Cu^{++} from H_2O by means of the cation exchanger, Zeo-Karb, and the anion exchanger, De-Acidite, is described. L. S. T.

Friedrich Wohler and his American pupils. H. S. van Klooster (*J. Chem. Educ.*, 1944, 21, 158—170). L. S. T.

Ernst von Meyer, 1847—1916. R. E. Oesper (*J. Chem. Educ.*, 1944, 21, 107—108). L. S. T.

Don José Celestino Mutis, 1732—1808. M. E. Weeks (*J. Chem. Educ.*, 1944, 21, 55). L. S. T.

XI.—GEOCHEMISTRY.

Waters from the Frio formation, Texas Gulf Coast. F. W. Jessen and F. W. Rolshausen (*Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1729, 16 pp.; *Petroleum Tech.*, 1944, 7, No. 3).—Analyses of 116 brines from various depths in a no. of oilfields in the area surveyed indicate variation in salinity with depth, with a possible max. concn. in the top 300 ft. of the Frio formation. D. D.

Metals in the stars. (Sit) H. S. Jones (*J. Inst. Metals*, 1944, 70, 175—196).—A lecture discussing our present knowledge of the composition of the sun, the stars, and interstellar space based on spectroscopic observations. A. R. P.

Temperature of the upper atmosphere. (Mme.) A. Vassy and E. Vassy (*J. Phys. Radium*, 1942, [viii], 3, 8—16).—The calculation of the temp. of the upper atm. from observations of ρ and composition, and of the polar auroræ, and from radioelectrical measurements, and the applicability of the formulæ of Laplace and of Chapman (A., 1931, 1350), relating pressure to altitude, are discussed. Temp. relations and the ionic composition of the ionised layers of the atm. are separately considered. Calculation of the temp. against altitude curves for temperate and polar latitudes indicates the importance of the direct absorption of light in the atm. thermal equilibrium. W. R. A.

Minerals new or rare to Britain. A. Russell (*Min. Mag.*, 1944, 27, 1—10).—A gold nugget (501.2 grains with quartz) was found in 1940 at Leadhills, Lanarkshire. Specks of Au have been found on russellite (A., 1938, I, 376) from Castle-an-Dinus wolfram mine, Cornwall. Other minerals described are: orpiment in clay from Clevedon, Somerset; semseyite from Carnarvonshire; dundasite from Cornwall and Carnarvonshire; wulfenite from Westmorland. L. J. S.

Crystal structure of gümbelite. E. Aruja (*Min. Mag.*, 1944, 27, 11—15).—Gümbelite forms fine flexible fibres (1 cm. long) perpendicular to the walls of fissures in slate on the shore of Lake Onega, Karelia. It is monoclinic with a 5.21, b 9.02, c 20.12 Å., β 96°, ρ 2.77. A similar X-ray pattern is given by the original gümbelite from Nordhalben, Bavaria. The mineral is compared with muscovite and hydromuscovite. L. J. S.

Mineral composition of the tin ores of Renison Bell, Tasmania. F. L. Stillwell and A. B. Edwards (*Proc. Austral. Inst. Min. Met.*, 1943, No. 131—2, 173—186).—The chief minerals in the ore-bodies are cassiterite, arsenopyrite, pyrite, and pyrrhotite, with quartz as the chief gangue mineral, accompanied by smaller amounts of tourmaline and topaz. Small amounts of chalcopyrite and stannite (I) accompany or follow these chief pyritic sulphides. Much of the gangue mineral of the late stages of crystallisation is a Mn-Fe-Mg

carbonate of varying composition (chemical analyses given). Minor and rare constituents of the lodes are wolfram, marcasite, magnetite, (I), tetrahedrite, jamesonite, canfieldite, pyrrargyrite, franckeite, and native Bi and Au. All these minerals and their mode of occurrence are described. The sequence of mineralisation, and the manner and rate of oxidation of the ores, which vary considerably with locality and composition, are discussed. L. S. T.

Petrology of two clastic dykes from the Placerville District, Colorado. J. C. Haff (*Amer. J. Sci.*, 1944, 242, 204—217). L. S. T.

Age of the Deccan traps of the Bombay and Salsette Islands. A. S. Kalapesi and R. N. Sukheswala (*J. Univ. Bombay*, 1944, 12, A, Part 5, 36—43).—The U and Pb contents of 9 rocks from different localities in these islands are recorded and used to calculate the age of the rocks by the well-known Pb, U, Th formula. The Th content is nil. The Deccan Traps belong to the Tertiary era. L. S. T.

Decomposed granite, Baton, Nelson. B. L. Taylor (*New Zealand J. Sci. Tech.*, 1943, 25, B, 78—86).—The geology of the decomposed granites and arkosic grits of the Baton district is outlined, and their prospecting and sampling described. Chemical analyses of the clay fractions and their behaviour on burning are recorded. Chemical analyses of granites and feldspars are also given. L. S. T.

Zircon in sedimentary rocks of Otago. F. J. Turner (*New Zealand J. Sci. Tech.*, 1943, 25, B, 89—90).—The distribution of zircon in the rocks of the Maniototo basin is discussed. The amount in Au-bearing deposits and the amount probably available from Au-mining operations are estimated. L. S. T.

Felspathic clay, Wyndham, Southland. R. W. Willett (*New Zealand J. Sci. Tech.*, 1943, 25, B, 87—88).—A bed of indurated clay interstratified in the basement rocks of the Wyndham district has the composition and physical properties of a stoneware clay. L. S. T.

Formation of colloid from halloysite in dilute acid solutions. P. G. Nutting (*J. Washington Acad. Sci.*, 1944, 34, 110—112).—Treatment of halloysite with dil. HCl at 96° forms a sol having the composition of allophane, $2\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 7\text{H}_2\text{O}$, after drying at 160°. A quant. relationship between sol formed and the HCl, clay, and H_2O used is given for certain ranges of [HCl]. L. S. T.

Some properties of brookite in the detritic formations of the Parisian Basin. (Mlle.) S. Duplaix (*Compt. rend.*, 1943, 217, 81—82).—The crystal form and optical properties of brookite found in the above formation are described. It is found only in small quantity, but is more stable than is usually supposed. A. J. M.

Regular inclusions of plagioclase in orthoclase (sanidine). A. Maucher (*Z. Krist.*, 1943, 105, 82—90).—Orthoclase (I) from Keban (Turkey) contains numerous inclusions of plagioclase (II). One surface of (II) always lies parallel to a surface of (I), and one or more edges of (II) are parallel to an edge of (I). This is difficult to explain since (II) is older than (I). A. J. M.

Etch figures of basal sections of quartz: their use in the orientation of water-worn crystals. F. N. Hanlon (*J. Proc. Roy. Soc. New South Wales*, 1944, 77, 40—51).—Results obtained by etching with HF sections of quartz cut perpendicular to the optic axis are recorded.

Measurement of densities [of minerals] by comparison with sand. A. Cailleux (*Compt. rend.*, 1943, 217, 30—31).—A method of estimating the d of minerals, by finding whether they sink or float in sand, is outlined. A vessel is partly filled with sand (grain size ~ 0.3 mm.), a fragment (3—7 mm. long) of the mineral is placed on the surface, and the vessel is gently shaken horizontally. After a few sec. minerals with $d >$ that of quartz remain on the surface; those with $d <$ that of quartz are submerged. The error is 1—2%. For success the sand must be neither too damp nor too dry, the fragments of mineral must be < 5 times as long as they are thick, and there is an optimum grain size for the sand. A. J. M.

Ilmenorutile from Sierra Leone. [L. C. Chadwick and T. Deans] (*Bull. Imp. Inst.*, 52, 45—47).—Ilmenorutile (I) is the chief constituent of an alluvial concentrate obtained from a locality near Sakasakala on the Tonkolili river. (I) crystallised apparently in intimate association with quartz. (I), ρ 4.74, has approx. TiO_2 55.7, Nb_2O_5 22.6, Ta_2O_5 9.4, FeO 11.0, total 98.7%. L. S. T.

Crystal structure of daubreelite. D. Lundqvist (*Arkiv Kemi. Min., Geol.*, 1943, 17, B, No. 12, 4 pp.).—X-Ray powder photographs show that daubreelite (FeCr_2S_4) has a spinel and not a pentlandite structure. C. R. H.

Discovery of nickel minerals in the argentiferous lead vein at Pontpean (Ile et Vilaine). H. Vincienne (*Compt. rend.* 1943, 216, 899—900).—Ni minerals are to be found in very fine fissures in the calcite of this vein. They consist of breithauptite (Ni antimonate) and rammelsbergite (Ni arsenate). A. J. M.

Radioactive substances. III. Analysis and age of a North Carolina monazite. A. D. Bliss (*Amer. J. Sci.*, 1944, 242, 327—330).—A monazite, ρ 5.18, from Spruce Pine, North Carolina, has Th 4.83, U 0.02, and Pb 0.13%. The age, calc. by the usual formula, is $\sim 6 \times 10^8$ years. L. S. T.

OCTOBER, 1944.

I.—SUB-ATOMICS.

Ground triplet in bromine II. K. R. Rao (*Current Sci.*, 1944, 13, 42).—The fundamental inverted triplet term $4p^3P$ of Br II, involving ~ 30 lines in the vac. grating region, has been established. The intervals are $4p^3P_2-4p^3P_1=3147$, and $4p^3P_1-4p^3P_0=695\text{ cm}^{-1}$. The identification of $5s^1D_5$ is corr. from 65657.1 to 61179.5 cm^{-1} .

N. M. B.

Absorption of the yellow line of the night sky by sodium vapour. J. Bricard and A. Kastler (*Compt. rend.*, 1943, 216, 878—880).—Na vapour absorbs the yellow line of the night sky completely if the temp. is sufficiently high. There is partial absorption when the v.p. corresponds to a temp. of 149° , and complete absorption at 209° .

A. J. M.

Experimental determination of the energies of atoms multiply ionised in deep levels, by crystal spectrography. (Mlle.) Y. Cauchois (*Compt. rend.*, 1943, 216, 801—804).— L spectra of heavy elements comprise frequencies which cannot be reconciled with the energy schemes of a singly ionised atom. These are satellites of more intense radiations, and five groups are recognised. The L satellites of heavy elements are, with few exceptions, of greater ν than the principal radiation. The three groups L_{α_1} , L_{β_2} , and L_{β_3} , which have their origin in the transitions $2p\ 3d-3d\ 3d$, $2p\ 3d-3d\ 4d$, and $2p\ 3d-3d\ 5d$, are examined, and by consideration of the structure of the doublets it is possible to arrive at the multiple-ionisation levels which give rise to them. Thus, if δ is the difference of ν of a satellite and the parent radiation, $\delta_{\alpha_1} = (2p\ 3d-3d\ 3d) - (2p-3d)$, $\delta_{\beta_2} = (2p\ 3d-3d\ 4d) - (2p-4d)$, $\delta_{\beta_3} = (2p\ 3d-3d\ 5d) - (2p-5d)$. If ΔL_{III} , ΔM_V , ΔN_V , and ΔO_V represent the energy differences of a state of the multiply ionised atom and that of the singly ionised atom, $\Delta M_V = \Delta L_{III} - \delta_{\alpha_1}$, $\Delta N_V = \Delta L_{III} - \delta_{\beta_2}$, $\Delta O_V = \Delta L_{III} - \delta_{\beta_3}$. To determine ΔL_{III} the curve showing variation of δ as a function of E for the different levels M_V , N_V , and O_V is drawn and extrapolated to $E = 0$. Vals. are given for Th, Ra, Bi, Pb, Tl, Au, and Pt.

A. J. M.

New data relative to atoms of atomic number 82 (Pb), 81 (Tl), and 79 (Au). Weak L -emission and outer levels. (Mlle.) Y. Cauchois (*Compt. rend.*, 1943, 216, 762—765; cf., A., 1942, I, 222, 349; 1944, I, 93).—The weak L emissions of Pb, Tl, and Au are investigated, and new data tabulated. The β_7 , β_7' , γ_8 , and γ_8' ($L_{II}N_{VII}$) doublets are resolved, and the vals. of O_I and N_{VII} , V_{II} are deduced.

A. J. M.

New light effect; intensity variation by direct photo-electric measurements. P. G. Deo (*Current Sci.*, 1944, 13, 44).—The instantaneous diminution Δz , by irradiation, of the conductivity of Cl_2 and other gases under electrical discharge is not a linear function of the corresponding light intensity I . $I-\Delta z$ curves obtained by varying the distance of the light source depend on the nature of the irradiation; the curve for violet may lie above or below the curve for white light, according to initial intensity.

N. M. B.

Physical principles of betatron. D. W. Kerst (*Radiology*, 1943, 40, 115—119).—Electrons with velocity which may be close to that of light are shot from an electron gun or injector into a circular path within a doughnut-shaped vac. tube and accelerated by increasing the intensity of the magnetic fields between the poles of the electromagnet enclosing the vac. tube. Orbit-expanding coils are not energised until after the electrons have been accelerated. The electrons travel through distances of up to 200 miles before striking the target and producing X-rays of energies 2.3 and $20 \times 10^6\text{ v}$. At the lower energy the X-rays tend to go forward in the direction which the electrons had when striking the target; at the higher energy an output of 50 r. per min. has been produced at 70 cm. A.C. is used.

E. M. J.

Electric breakdown and cumulative ionisation. B. Davidov (*J. Physics U.R.S.S.*, 1943, 7, 196).—Mathematical.

W. R. A.

New spiral form of the periodic table. E. I. Emerson (*J. Chem. Educ.*, 1944, 21, 111—115).—The elements are arranged in the natural sequence of at. nos. on a plane spiral. The arrangement reflects the periodic occurrence of similar outer orbital configurations and the periodic occurrence of properties.

L. S. T.

Energies and periods of α -disintegrations. I. Energies. II. Periods. A. Berthelot (*J. Phys. Radium*, 1942, [viii], 3, 17—28, 209

M (A., I.)

52—56).—I. The energy of α -disintegration of the natural radioactive elements is considered as a function of the no. of nuclear constituents. Using energy vals. for the β -disintegrations, the energy of binding of the last neutron to enter the nucleus is calc. for all isotopes having at. nos. 82—84. For at. nos. 82 and 86, discontinuities in the binding energy of neutrons occur when the no. of neutrons in the nucleus exceeds 126 and 134; for at. no. 82 the discontinuity is $\sim 2.4\text{ Me.v}$. The emission of energetic photons by Ra-C'' and Th-C'' depends on this discontinuity.

II. The frequency of α -disintegration of the natural radioactive elements is considered as a function of the energy change involved, the elements being grouped into families of isotopes. Evaluation of nuclear radii from these data leads to vals. intermediate between those of Gamow and those of Bethe. The significance of the energy-period relationship is discussed with reference to the fine structure of nuclei.

W. R. A.

Complexity of γ -radiation from Ra-D. S. T. Tsien (*Compt. rend.*, 1943, 216, 765—767).—To verify the results of Amaldi *et al.* (*Ric. Sci.*, 1939, 10, 111) who showed that, contrary to former work, the γ -radiation from Ra-D is complex, the radiation is examined by means of an ionisation chamber filled with Ne at atm. pressure. This favours weak γ -rays because of its high coeff. of absorption. Secondary β -rays produced in the gas are completely absorbed. To distinguish rays of approx. the same energy, absorbents of rare-earth oxalates are used. The γ -radiation from Ra-D contains a ray (ray B) of energy $42.00-43.54\text{ ke.v}$. The principal γ -ray of Ra-D (ray A) has energy $43.54-46.86\text{ ke.v}$. The intensity ratio $I_A/I_B = 12 \pm 7$. $I_A = 3.8 \pm 0.8\gamma$, $I_B = 0.3 \pm 0.2\gamma$ per 100 disintegrations.

A. J. M.

Determination of radioactive period of vanadium of mass 52. J. Martelly (*Compt. rend.*, 1943, 216, 767—769; cf. Amaldi *et al.*, A., 1935, 910; Walke, A., 1938, I, 8).—The period of ^{52}V obtained by the reaction $^{61}\text{V} (n, \gamma) ^{52}\text{V}$, by irradiating V_2O_5 with slow neutrons, is $3.74 \pm 0.01\text{ min}$.

A. J. M.

Determination of energy of γ -rays from the radioactive isotope of vanadium ^{52}V . J. Martelly (*Compt. rend.*, 1943, 216, 838—840).—The energy of γ -rays emitted from ^{52}V , determined by measuring the coeff. of absorption in Pb, Fe, and Cu, is $1.45 \pm 0.05\text{ Me.v}$. (cf. Yuasa, A., 1944, I, 94).

A. J. M.

Apparatus for counting electrons of small energy. Application to ^{80}Br (18 min.). A. Berthelot (*Compt. rend.*, 1943, 216, 806—808).—Absorption of electrons from ^{80}Br is very weak and shows no discontinuities, indicating the absence of conversion electrons of low energy. (Cf. C., 1944, Part 4.)

A. J. M.

Investigation, by the absorption method, of radiation due to internal conversion, emitted by ^{82}Br (34 hr.) and $^{80}\text{Br}^*$ (4.5 hr.). A. Berthelot (*Compt. rend.*, 1943, 216, 884—886).—Apparatus previously described (cf. preceding abstract and C., 1944, Part 4) has been used to investigate conversion radiation associated with the transition $^{80}\text{Br}^* \rightarrow ^{80}\text{Br}$ (18 min.). The thicknesses of Al absorbents required are 0.38, 0.95, 2.05, and 3.75 mg. per sq. cm., corresponding to energies determined by Valley *et al.* (A., 1939, I, 294) and to the Auger electrons. Using these energies the internal conversion energies of ^{82}Br (34 hr.) are 34 and 53 ke.v.

A. J. M.

Cosmic rays. (Mlle.) T. Grivet (*Ann. Physique*, 1943, [xi], 18, 73—134).—A detailed experimental analysis is reported. Measurements are made at and below sea-level of the proportion of hard and soft rays, Rossi curves are traced, and the angle between rays in clusters is determined. Radiation which penetrates large thicknesses of earth consists of heavy electrons or mesons; the electrons are produced by decomp. of mesons in their passage through air or earth and by collisions of mesons with the atoms of dense screens.

N. M. B.

Separation of electronic and non-electronic components of cosmic radiation by Bhabha's method. S. V. C. Aiyar (*Proc. Indian Acad. Sci.*, 1944, 19, A, 177—181).—The theoretical prediction of Bhabha (A., 1944, I, 163) that Pb is more effective in cutting out electrons if split in the ratio $\sim 1:4$ (the thinner piece being used for shower production from high-energy electrons and the thicker piece absorbing the low-energy electrons) has been confirmed experimentally by observations at Ootacamund (geomagnetic latitude 1.7° N ., 7200 ft. above mean sea level). Two Pb filters of total thickness 5.25 cm .

and five counters, three connected in coincidence and the other two in parallel and in anti-coincidence, were used; the total wt. of the apparatus was 4 oz. The hard component constitutes 66.3% of the total intensity. W. R. A.

Scattering of charged mesons under the influence of radiation damping. S. T. Ma and C. F. Hsieh (*Proc. Camb. Phil. Soc.*, 1944, 40, 167—172).—An alternative derivation of Waller's integral equation is given. The theoretical treatment of the scattering of charged vector mesons (A., 1944, I, 27) is extended to pseudoscalar mesons. H. J. W.

Representation of corpuscular interactions by means of a particle of spin 1. G. Petiau (*Compt. rend.*, 1943, 218, 832—834).—Mathematical. A. J. M.

II.—MOLECULAR STRUCTURE.

Vibration frequencies of certain molecular groups (near infra-red). P. Barchewitz (*Ann. Physique*, 1943, [xii], 18, 167—189).—Certain bands in the near infra-red can be attributed, as a first approximation, to the presence of mol. groups (OH, NH₂, NH, CH₃, CH₂, etc.). Conditions exist under which the bands characteristic of these groups are not revealed, and by modifying the experimental conditions (variation of temp., dilution, etc.) the max. reappear only in certain cases. From the data, considerations on mol. structure are deduced and discussed. N. M. B.

Ultra-violet absorption spectrum of diamond. (Mrs.) K. S. Bai (*Proc. Indian Acad. Sci.*, 1944, 19, A, 253—260).—The ultra-violet absorption spectra in the region 3300—2200 Å. have been investigated. With non-fluorescent and yellow-green-fluorescent diamonds the recorded spectra extend to 2250 Å., requiring, however, long exposure with yellow-green-fluorescent specimens. Weakly blue-fluorescent diamonds show a cut-off at 3050 Å., preceded by three sharp and intense bands at 3060, 3075, and 3157 Å. In strongly blue-fluorescent diamonds these bands disappear, and the region of transmission extends to 2450 Å., with step-like falls in intensity at 2845, 2715, and 2570 Å. Diamonds exhibiting both types of fluorescence give absorption lines at 2359 and 2356 Å., with five bands at greater and three at shorter λλ. Intensity of fluorescence varies with the intensity and breadth of these absorption lines and bands, which sharpen and shift towards shorter λλ at liquid-air temp. W. R. A.

Ultra-violet transparency patterns in diamond. G. R. Rendall (*Proc. Indian Acad. Sci.*, 1944, 19, A, 293—297).—The ultra-violet transparency of crystals and cleavage plates of diamonds is examined by passing 2536 Å. Hg radiation through the specimen and producing an image in a screen of U glass. A wide range of behaviour, from complete opacity to complete transparency, related to the luminescence properties of the individual diamond, has been observed. Transparency patterns of cleavage plates are in some cases similar to the luminescence patterns, but reversed; in other cases such a resemblance is not observed. The origin of these differences and similarities is discussed with reference to the intrusion of one diamond structure into another. W. R. A.

Relations between chemical activity and absorption in the ultra-violet of certain organic molecules. VIII. Absorption spectra of monochloro-derivatives of the amides of acetoacetic acid. IX. Absorption spectra of the isonitro-derivatives of the amides of acetoacetic acid. K. G. Naik, R. K. Trivedi, and B. N. Mankad (*J. Indian Chem. Soc.*, 1943, 20, 407—408, 414).—VIII. Absorption is increased and shifted towards the visible by introduction of Cl into the CH₂ group of the anilide, *m*-4-xylylamide, and α -naphthylamide of CH₃Ac·CO₂H.

IX. Conversion of the CH₂ group into C:N·OH in the same amides produces a marked shift of absorption towards the visible and a smoothing out of the absorption max. L. J. J.

Absorption spectra of the simplest coloured compounds. A. Schwarzenbach, K. Lutz, and E. Felder (*Helv. Chim. Acta*, 1944, 27, 576—584).—The extinction coeffs. of solutions of a no. of simple coloured compounds are measured at various λλ and the λ of the absorption max. is compared with the vals. $k'_p\sqrt{n+k''_p}$ and $k'n+k''_p$ ($k'_p, k''_p, k'_e, k''_e = \text{const.}$, $n = \text{no. of double linkings in the mol.}$) for polyene compounds and compounds with two canonical resonance forms, respectively. J. W. S.

Spectrographic and kinetic study of the alkaline fading of tetra-iodophenolsulphonaphthalein. E. S. Amis and T. Overman (*J. Amer. Chem. Soc.*, 1944, 66, 941—945).—The absorption of alkaline-faded iodophenol-blue approximates to that of alcohol, acids, and H₂O, as would be expected if the carbinol is formed during fading. Spectra of the unfaded and regenerated acid solution are identical and the fading process, therefore, appears to be reversed in acid solution. The absorption band is not shifted but only lowered in intensity during fading. Addition of NaI influences the kinetics of fading by the Brønsted primary salt effect. Fading thus appears to consist of transformation from the quinonoid to the carbinol structure. W. R. A.

Ultra-violet absorption spectrum of ibogaine. V. Brustier, D. Vincent, and (Mlle.) I. Sero (*Compt. rend.*, 1943, 216, 909—911).—The ultra-violet absorption spectrum of ibogaine, the active principle of *Tabernanthe iboga*, shows marked similarity with that of quinoline. There is also a much weaker resemblance to the spectrum of indole, although chemical evidence (Raymond-Hamet, *Bull. Soc. chim.*, 1942, [v], 9, 620) seems to indicate the existence of an indole nucleus in this alkaloid. The mol. probably contains a quinoline or iso-quinoline nucleus and may also contain a subsidiary indole nucleus, the effect of the latter on the absorption spectrum being masked. A. J. M.

Hertzian spectra of solutions of alcohols. P. Girard and P. Abadie (*Compt. rend.*, 1943, 218, 836—838).—If a long-chain alcohol is diluted with various non-polar liquids (C₆H₆, C₈H₁₈, vaseline), study of the Hertzian spectrum shows that the mol. undergoes a profound change of geometrical form, varying with the diluent. The alcohol mol. appears to be very plastic and is readily deformed by hydrocarbon mols. The spectrum of solutions of *n*-C₈H₁₇·OH shows three clearly defined regions of dispersion, whereas that of the pure alcohol shows only two. The geometrical model of the mol. passes from an ellipsoid of revolution in the case of the pure alcohol, to an ellipsoid with three unequal axes in the case of solutions. The deformation is least marked in vaseline, probably because of its large mol. vol. The ratio of relaxation times indicates that the alcohol mol. is probably more extended in C₈H₁₄ than in vaseline. Dilution of the alcohol by C₆H₁₄ or C₈H₈ displaces the regions of dispersion towards short λ. This displacement is not $\propto \eta$ as required by Debye's theory. The spectrum of the alcohol in vaseline makes it clear that the η involved in dispersion is not that which is ordinarily measured. A. J. M.

Fluorescence and absorption spectra of diamond in the visible. (Miss) A. Mani (*Proc. Indian Acad. Sci.*, 1944, 19, A, 231—252).—Fluorescence and luminescence spectra in the visible have been investigated at room and liquid-air temp. for 32 diamonds of widely varying luminescence colour and intensity. The spectra are related with respect to both their general character and their intensities. All the spectra consist mainly of the electronic bands at 4152 and 5032 Å., which comprise a set of lines, bright in fluorescence, dark in absorption, and lattice lines, appearing at greater λ in fluorescence. With blue fluorescence the 4152 Å. system is the more prominent, and with yellow fluorescence, the 5032 Å. system, but, generally, the two systems appear with comparable intensities. 36 electronic lines, other than 4152 and 5032 Å., are recorded. The 4152 Å. line appears in most diamonds as a doublet, the width and separation of the two lines increasing with intensity of blue fluorescence. The 5032 Å. line shows no such changes. Differences in ν between the main lines at 4152 and 5032 Å. and the associated lattice lines lie in the infra-red and represent the vibration ν of the diamond lattice. $\Delta\nu$ are the same in both systems, but the degree of sharpness and intensity distribution vary. 25 ν are derived, constituting the lattice spectrum of diamond. W. R. A.

Fluorescence of naphthalene crystals. I. V. Obreimov and C. G. Schabaldas (*J. Physics U.R.S.S.*, 1943, 7, 168—178).—The fluorescence spectrum of cryst. C₁₀H₈ has been investigated at 20° K. It is similar to the resonance spectrum of gases, and contains practically all the Raman and some non-Raman vibrational ν . Four electronic transitions were found. W. R. A.

Theory of the influence of concentration on the fluorescence of solutions. S. I. Vavilov (*J. Physics U.R.S.S.*, 1943, 7, 141—152).—A migration of energy between mols. must occur if there exists a quantum-mechanical resonance between the excited and non-excited mols. in a solution; when the distances between them are great the migration will lead to depolarisation. At small distances when there is considerable resonance coupling between mols. the migration may be accompanied by noticeable quenching of fluorescence. The theory of the influence of concn. on fluorescence is developed and formulae are given for the yield, degree of polarisation, and lifetime of the excited state which are confirmed by the available experimental data. W. R. A.

Influence of temperature on the quenching of active nitrogen at various pressures. S. S. Joshi and A. Purushotham (*Proc. Indian Acad. Sci.*, 1944, 19, A, 159—162).—Quenching of the afterglow of active N is dependent on temp. and occurs at a definite temp., which is the higher the higher is the streaming pressure of the gas. Vals. at 15 and 33 mm. Hg are 215° and 330°. Existence of a chemically active form of N, which exhibits no afterglow, is considered improbable. W. R. A.

Mechanism of luminescence of phosphors. II. V. V. Antonov-Romanovski (*J. Physics U.R.S.S.*, 1943, 7, 153—167).—Using the experimental observation that the displacement of a thermal electron of the KCl + Tl phosphor between two consecutive trapings is small and of the order of the lattice const. (A., 1943, I, 114; 1944, I, 3), a theory of recombination luminescence is developed. This theory explains the shape of the decay curve and its dependence on conditions of excitation and decay, and is used to estimate the magnitudes of the diffusion coeff. and the mobility of the electrons.

tert. alcohols, and more particularly position vals. of CH₃ in alkyl chains, are given. Modifications in the bubbler for measuring γ are described.

VII. Vals. of ρ , γ , and parachor of 13 paraffin hydrocarbons are given. Parachor vals. are given for CH₄ (40), H (15.5), and C (9.0). The val. for CH₂ is not changed by chain length up to C₁₂H₂₆. Chain-branching does not produce uniform effects, but the data are inadequate to evaluate variations in the effect.

W. R. A.

III.—CRYSTAL STRUCTURE.

Method of calculating the integral breadths of Debye-Scherrer lines: generalisation to non-cubic crystals. A. R. Stokes and A. J. C. Wilson (*Proc. Camb. Phil. Soc.*, 1944, 40, 197—198).—An extension of work previously reported (A., 1942, I, 318).

H. J. W.

Scattering of X-rays in polycrystalline substances. I. [Theory.] II. Application to liquids. L. M. Brechovskich (*J. Physics U.R.S.S.*, 1943, 7, 179—188, 189—191).—I. A theory of X-ray scattering by polycryst. substances is developed which takes into account the thermal vibrations of atoms. The ratio of the intensity of the scattered radiation to the Laue part is $>$ for single crystals and the Debye background depends on the size of the grain in the same way as the scattered radiation.

II. An extension of the theory to liquids, based on the concept of the liquid as a finely-powdered polycryst. specimen, has been made and is applied with fair success to liquid Na.

W. R. A.

X-Ray topographs of diamond. G. N. Ramachandran (*Proc. Indian Acad. Sci.*, 1944, 19, A, 280—292).—Topographic maps representing the variation in intensity of X-ray reflexion over the area of a crystal plate are obtained by photographing the Laue reflexion from any set of crystal planes. White X-radiation, diverging from a pin hole, is used. Lateral distortion of the particular Laue spot examined is eliminated by tilting either the photographic or the crystal plate. Topographs of 18 cleavage plates of diamond are given and are of three types: (i) those exhibiting a uniform distribution of relatively weak reflexion intensity over the whole area and characteristic of the blue-fluorescent diamonds which are opaque in the ultra-violet and show no birefringence; (ii) those having a strong reflexion intensity and showing parallel lines running in different directions over the whole crystal area (ultra-violet-transparent non-luminescent diamonds showing an intense birefringence are characteristic of this group); (iii) an apparent co-existence of types (i) and (ii), giving a uniform weak reflexion overlaid by some regions of intense reflexion. The latter appear as small areas of uniformly high intensity, as a few fine streaks running through the crystal, or as a combination of these two effects. Type (iii) has properties intermediate between those of types (i) and (ii). Correlations with luminescence, ultra-violet transparency, and birefringence patterns confirm the suggestion that type (i) belongs to the tetrahedral structure, type (ii) to the octahedral, and type (iii) is an interpenetration of the tetrahedral and octahedral types.

W. R. A.

X-Ray reflexion and structure of diamond. G. N. Ramachandran (*Proc. Indian Acad. Sci.*, 1944, 19, A, 304—309).—Laue photographs, taken with the X-ray beam normal to the (111) planes, have been investigated for two blue-fluorescent diamonds with greatly different fluorescence intensities but similar in other respects. Microphotometric determination of the peak intensity of the various spots shows that, although the intensity is greater for the fluorescent diamond, the intensity ratio (r) of the various spots differs. ($r - 1$) \propto the product of the structure factor, the λ reflected, and a function of the angle of incidence.

W. R. A.

Intensity of X-ray reflexion of diamond. P. S. Hariharan (*Proc. Indian Acad. Sci.*, 1944, 19, A, 261—264).—The intensity of X-ray reflexion from the (111) planes of several diamonds is studied. With blue-fluorescent diamonds the intensity of X-ray reflexion increases with intensity of fluorescence, whereas with yellow-green-fluorescent diamonds the reverse is shown. The order of intensity of X-ray reflexion is: non-fluorescent $>$ yellow $>$ blue. This behaviour is correlated with the views advanced by Raman (see below) on the crystal structure of real diamonds.

W. R. A.

Experimental evidence for the existence of the four possible types of diamond. R. S. Krishnan (*Proc. Indian Acad. Sci.*, 1944, 19, A, 298—303).—X-Ray and spectroscopic studies of diamond provide experimental evidence for the existence of four diamond structure types. Co-existence of the two tetrahedral types is inferred from the increased intensity of X-ray reflexion in such diamonds. The Bragg reflexions of a diamond consisting of alternate layers of the two octahedral types, examined by the oscillating-crystal method, exhibited a periodicity consistent with a difference of 0.05% in crystal spacing of the two types. The Raman displacement corresponding with the fundamental lattice vibration shows, for the octahedral type of diamond, a width equal in order of magnitude to the expected vibration frequency difference of the two octahedral structures.

W. R. A.

Crystal symmetry and structure of diamond. (Sir) C. V. Raman (*Proc. Indian Acad. Sci.*, 1944, 19, A, 189—198).—The C atoms in diamond may be oriented in space in four different ways, positive or negative tetrahedral or octahedral forms. A fundamental vibration of the diamond lattice, $\nu = 1332$ cm.⁻¹, should appear in both Raman and infra-red spectra if the crystals are tetrahedral, but only in the Raman spectrum if the crystals are octahedral. This behaviour has been observed in the common (tetrahedral) and rarer (octahedral) types by Robertson *et al.* (A., 1934, 583). The two tetrahedral types have identical properties and interpenetrate freely, but composition planes result from the intertwinning of the two octahedral forms, appearing as a lamellar structure parallel to the octahedral planes. Inter-twinning of octahedral and tetrahedral forms may also exist.

W. R. A.

Crystal forms of the Panna diamonds. S. Ramaseshan (*Proc. Indian Acad. Sci.*, 1944, 19, A, 334—342).—The external forms and surface characters of 29 Panna diamonds have been examined. The surfaces of the crystals are divided into 24 segments of sharply defined edges. In the best specimens these segments are triangles, the edges meeting at points and vertices in groups of four and six. Measurements of curvature show that this is highly variable, even in an individual diamond.

W. R. A.

X-Ray studies on orthorhombic lead monoxide. A. Bystrom (*Arkiv Kemi, Min., Geol.*, 1944, 17, B, No. 8, 6 pp.).—From X-ray measurements by the powder method the lattice dimensions of orthorhombic PbO are a 5.48, b 4.74, c 5.88 Å., in accord with the measurements of Halla and Pawlek (A., 1927, 924) but, contrary to their interpretations, evidence is obtained that the Pb atoms are arranged in approx. face-centred positions, and each O atom in contact with three others, yielding a structure with sheets of Pb atoms in the (001) plane and puckered O layers in every second interspace. This provides three O atoms linked by coordinate linkings to the Pb and with the 2s electrons of the latter completing an octet of electrons around the Pb atom. The space-group is probably —Pba. Hydrated PbO, prepared by hydrothermal synthesis at 270°, is orthorhombic with a 14.08, b 5.71, c 8.70 Å. and space-group probably either D_{2h}^{16} or

J. W. S.

X-Ray analysis of antimony trifluoride. A. Bystrom and A. Westgren (*Arkiv Kemi, Min., Geol.*, 1943, 17, B, No. 2, 7 pp.).—Crystals of SbF₃ are orthorhombic, with 4 mols. per unit cell, space-group C_{2v}^{10} —Ama. Each Sb is situated on top of an approx. equilateral triangle of F atoms. Parameters have been derived: Sb—F 2.0 Å. within a mol.; three other F, each belonging to different mols., neighbour each Sb, two at 2.55 and one at 2.92 Å. Sb—F angles are 81.9° (one) and 104.3° (two). F—F distances from mol. to mol. are 2.73, 2.73, and 2.99 Å.

W. R. A.

Crystal structure of ZnSb₂O₄ and isomorphous compounds. S. Ståhl (*Arkiv Kemi, Min., Geol.*, 1943, 17, B, No. 5, 7 pp.).—MgSb₂O₄, MnSb₂O₄, FeSb₂O₄, CoSb₂O₄, NiSb₂O₄, and ZnSb₂O₄ were prepared by heating the metallic oxides with Sb₂O₃ or the metal with Sb₂O₄ in a vac. The lattice consts. of these compounds as determined by the powder method are recorded. ZnSb₂O₄ has a structure similar to that of Pb₃O₄ with space-group —P4₁/mbc.

J. W. S.

X-Ray analysis of CrVO₄ and isomorphous compounds. K. Brandt (*Arkiv Kemi, Min., Geol.*, 1943, 17, A, No. 6, 13 pp.).—CrVO₄ is orthorhombic with space-group D_{2h}^{16} —Cmc₂m. The unit cell has a 5.568, b 8.208, and c 5.977 Å. and contains 4 mols. The Cr atoms are surrounded by distorted octahedra of O atoms, which, sharing two edges with each other, form long, slightly staggered strings parallel with the (001) plane. These strings are bound together by forming slightly irregular tetrahedra of O atoms around the V atoms. NiCrO₄, CoCrO₄, CuCrO₄, ZnCrO₄, and CdCrO₄ have a similar structure and their lattice consts. are recorded.

J. W. S.

Tungsten oxides.—See A., 1944, I, 183.

Oxygen positions in tungstates and molybdates with the scheelite structure. L. G. Sillén and (Miss) A. L. Nylander (*Arkiv Kemi, Min., Geol.*, 1943, 17, A, No. 4, 24 pp.).—On the assumption that the ions are rigid spheres, parameters of isomorphous compounds MXO₄ (M = Ca, Sr, Pb, Ba; X = W, Mo), crystallising in the space-group C_{4v}^8 , are deduced which agree well with experimental vals. These derived vals. give insight into which interat. contacts are really essential to the stability of the lattice. Applications of the method to other structures are suggested.

W. R. A.

X-Ray analysis of twinned MnP crystals. K. E. Fylking (*Arkiv Kemi, Min., Geol.*, 1943, 17, A, No. 7, 9 pp.).—X-Ray investigation by the powder method indicates that MnP is orthorhombic, with a 5.905, b 5.249, c 3.167 Å. The ρ (5.49) corresponds to 4 MnP mols. per unit cell. Rotation X-ray diffraction photographs with single crystals in some cases show additional lines attributable to twinning.

J. W. S.

Structure of natrophilite, NaMnPO₄. A. Bystrom (*Arkiv Kemi, Min., Geol.*, 1943, 17, B, No. 4, 4 pp.).—X-Ray investigations by the powder method indicate that the most probable space-group of NaMnPO₄ is D_{2h}^{16} —Pnma. The cell dimensions are a 10.52, b 6.32, and c 4.97 Å.

J. W. S.

Crystal structure of Ni₂Mo. D. Harker (*J. Chem. Physics*, 1944, 12, 315—317).—A Ni-Mo alloy containing ~20 at.-% Mo exists as a cubic close-packed structure at temp. >900°. Quenching and annealing at <840° leads to a slight tetragonal distortion of the cubic structure. The resulting tetragonal cell has 2.5 times the vol. of the distorted face-centred cubic cell, and corresponds to space-group C_{4h}^{2v} -I4/m, unit cell a_0 5.720, c_0 3.564 Å., c_0/a_0 0.6231, with 2 Mo in 2(a), 8 Ni in 8(h), $x = 0.200$, $y = 0.400$. L. J. J.

Binary system Cd(Hg(CNS))₂-Co(Hg(CNS))₂.—See, A. 1944, I, 221.

Structure of collagen fibres.—See B., 1944, II, 226.

Structure of wool fibre.—See B., 1944, II, 225, 226.

Electron diffraction of sulphur nitride, arsenic disulphide (realgar), arsenic trisulphide (orpiment), and sulphur. C. S. Lu and J. Donohue (*J. Amer. Chem. Soc.*, 1944, 66, 818—827).—From electron diffraction measurements the S₈ mol. has a regular puckered ring with S—S 2.07±0.02 Å. and angle S—S—S 105±2°, and shows rather large amplitude of thermal vibrations; As₂S₃ has As—S 2.25±0.02 Å., angles As—S—As 100±2° and S—As—S 114±2°. Mol. structures of As₂S₃ and S₈N₄ could not be unequivocally established, but cradle-shaped configurations of an alternating eight-ring are satisfactory. In S₈N₄ there is a bisphenoid of S and a square of N atoms with N—S 1.62±0.02, S—S 2.69 Å., angles S—N—S 112° and N—S—N 106°, whereas As₂S₃ has a bisphenoid of As and a square of S atoms with As—S 2.23±0.02, As—As 2.49±0.04 Å. and angles As—S—As 101±4°, S—As—S 93°, and S—As—S 100°. The structures, and more particularly those of As₂S₃ and S₈N₄, are discussed in relation to their chemical properties. W. R. A.

Magnetic susceptibility of diamond. A. Sigamony (*Proc. Indian Acad. Sci.*, 1944, 19, A, 310—314).—The magnetic susceptibility, χ , of 40 Indian and S. African diamonds was determined by the Curie method. No systematic changes in χ with changes in colour, absorption, luminescence, and photoconductivity were observed. Vals. of χ ranged between -0.456 and -0.411×10^{-6} . No change in χ was observed when two highly fluorescent diamonds were exposed to intense radiation from a C arc, filtered free from infra-red. W. R. A.

Magnetic susceptibility and anisotropy of carborundum. A. Sigamony (*Proc. Indian Acad. Sci.*, 1944, 19, A, 377—380).—The magnetic susceptibility, χ , and the anisotropy of SiC have been investigated by the Curie method. Black crystals are diamagnetic but show irregular behaviour. A green, translucent, hexagonal plate of SiC behaved regularly and gave $\chi = -12.8 \times 10^{-6}$ and anisotropy 0.82×10^{-6} . W. R. A.

Principal magnetic susceptibilities of metal crystals. S. R. Rao (*Current Sci.*, 1944, 13, 125—126).—Determinations of χ_{11} and χ_{12} on single crystals of Bi, Zn, Cd, and Te by Krishnan's torsional method (A., 1935, 924) give, respectively: Bi -1.058 , 1.495 ; Zn -0.206 , -0.147 ; Cd -0.234 , -0.169 ; Te -0.342 , -0.289 (all $\times 10^{-6}$), in agreement with existing published vals. by other methods. L. J. J.

Photoconductivity of diamond. I. Experimental. II. Theoretical. D. D. Pant (*Proc. Indian Acad. Sci.*, 1944, 19, A, 315—324, 325—333).—I. The photoconductivity of 36 diamonds, mostly polished cleavage plates, has been measured with Hg illumination parallel and perpendicular to the polished plane faces. The diamonds fall into three poorly-defined groups giving photocurrents of 10^{-8} , 10^{-9} , and 10^{-10} amp. No clear-cut division into diamonds of high and low conductivity, as suggested by Robertson *et al.* (A., 1934, 583), is possible. Diamonds highly photoconducting in the ultra-violet exhibit similar properties in the visible. Strongly photoconducting diamonds exhibit the red-light effect but this is not observed with lower photoconductivities. Such diamonds also exhibit a secondary current on long illumination which persists after the light is extinguished. Illumination with red light increases the current when the diamond is in this state, the increase being quantitatively related to the magnitude of the secondary current without illumination. The relations between photoconductivity and other optical properties are discussed.

II. Variations in photoconductivity in diamonds are due to variations in crystal structure, assuming that non-homogeneities and irregularities in the crystal produce the photoelectrically active centres. Other features of photoconductivity, e.g., the spectral distribution curves (particularly the rise for $\lambda\lambda < 3000$ Å.), the absence of a definite threshold frequency, the effect of red light, and the secondary current, are explained. The relation between the magnitude of the dark secondary current and that produced by red-light excitation is derived theoretically. W. R. A.

Lattice spectrum and specific heat of diamond. B. Dayal (*Proc. Indian Acad. Sci.*, 1944, 19, A, 224—230).—The bulk modulus of diamond, calc. from the spectroscopic data of Krishnan (A., 1944, I, 213) and of Mani (*ibid.*, p. 212) by the method of Nath (A., 1935, 1058), is 5.9×10^{12} , in good agreement with experimental vals. Vals. of C_v have been calc. from spectroscopic data, the three degrees of freedom not covered by these data being considered as an elastic spectrum and represented by a term of the Debye type having a

characteristic temp. of 820°. Observed and calc. vals. agree well, particularly in the range 200—1100° K. W. R. A.

Nature and origin of the luminescence of the diamond. (Sir) C. V. Raman (*Proc. Indian Acad. Sci.*, 1944, 19, A, 199—215).—The luminescence of several specimens of Indian and S. African diamonds, both natural crystals and cleavage plates, has been studied. Many cleavage plates show luminescence patterns which, together with the transparency patterns in the ultra-violet at $\lambda < 3000$ Å. and the patterns of structural birefringence between crossed polaroids, are due to the lamellar twinning of the various crystal structures of diamond (cf. A., 1944, I, 216). Interpenetration of the positive and negative tetrahedral forms results in a blue luminescence without structural birefringence and opacity to ultra-violet radiation. Interpenetration of tetrahedral and octahedral structures gives rise to a yellow luminescence, a banded structural birefringence, and imperfect ultra-violet transparency. Interpenetration of the two octahedral forms gives no luminescence, but produces ultra-violet transparency and a characteristic finely-streaked birefringence. The emission and absorption spectra in the visible region, and the reflecting power of the lattice planes for X-rays, confirm the physical nature of the luminescence. W. R. A.

Evaluation of the specific heat of rock salt by the new crystal dynamics. B. Dayal (*Proc. Indian Acad. Sci.*, 1944, 19, A, 182—187).—By the Raman dynamics of crystal lattices the rock salt structure has nine distinct ν of vibration, representing 45 of the 48 degrees of freedom of the 8 Na⁺ and 8 Cl⁻ ions in a super-lattice cell. These ν are evaluated and agree well with the experimental vals. from the Raman spectrum. The other three degrees of freedom representing the spectrum of the elastic vibrations of the lattice are calculable from known elastic consts. Vals. of C_v calc. from these data agree satisfactorily with experimental vals. W. R. A.

Birefringence patterns in diamond. (Sir) C. V. Raman and G. R. Rendall (*Proc. Indian Acad. Sci.*, 1944, 19, A, 265—273).—The structural or geometric birefringence of several diamonds is investigated. This birefringence results from the co-existence in the crystal of structures with different properties and crystal spacings. Diamonds of the blue-luminescent, ultra-violet-opaque type are isotropic, whereas those of the non-luminescent, ultra-violet-transparent type exhibit birefringence. X-Ray studies point to a difference in crystal spacing between the two octahedral structure types present in the non-luminescent diamonds, which results in the laminar birefringence of such diamonds. The production of birefringence patterns by the intrusion of the octahedral type structure into diamonds having tetrahedral structure is confirmed by variations of luminescence, ultra-violet transparency, and X-ray reflexion over the specimen. W. R. A.

Luminescence patterns in diamond. K. S. Bai (*Proc. Indian Acad. Sci.*, 1944, 19, A, 274—279).—The patterns of intensity and colour in the luminescence of cleavage plates of diamond, produced by long-wave ultra-violet illumination, are studied. Lines in the pattern frequently run parallel to the natural faces of the crystal. Blue-luminescent diamonds may show no pattern, whereas patterns are always observed with mixed blue and yellow luminescence. Yellow luminescence is characterised by several bright parallel lines, sometimes in > one direction. Local variations in the ultra-violet absorption spectrum show that the patterns arise from the intrusion of a diamond structure having properties different from those of the rest of the crystal. W. R. A.

Variation of birefringence of gypsum and barytes with temperature. J. Jaffray (*Compt. rend.*, 1943, 216, 814—816).—For gypsum, the birefringence (b) of cleavage laminae is a linear function of temp., and $db/d\theta$ is negative, decreasing regularly with decreasing λ between 8500 and 3500 Å. For barytes cut perpendicularly to the acute bisector of the optic axes, the birefringence is also a linear function of temp., but $db/d\theta$ is positive and increases as λ decreases over the range 9000—3800 Å. A. J. M.

Photodichroism of thin coloured sheets of sodium chloride. S. Nikitine (*Compt. rend.*, 1943, 216, 758—760).—A section of synthetic NaCl crystal, initially colourless, coloured by irradiation with X-rays for the first time, shows photodichroism when exposed to rectilinearly polarised white light. If the same section, partly decolorised and rendered anisotropic by the action of the polarised white light, is to be used again for the same experiment, it must first be completely decolorised, and then re-coloured by X-rays. It will then show the photodichroism again, and this can be repeated indefinitely. However, after each treatment the crystal shows a fatigue effect, evidenced by a decrease in the photodichroism, although the crystal is submitted to identical conditions. To study this in greater detail, the effect of irradiating coloured crystals with polarised monochromatic light preferentially absorbed by the F centres (blue light) or the F' centres (yellow and orange light) has been investigated. It is thus shown that a crystal showing fatigue contains both F and F' centres, whilst a new crystal contains only F centres. The fatigue effect is due to the production of an increasing no. of F' centres on each exposure of the crystal to X-rays.

Thermodynamics of crystal lattices. IV. Elastic constants of a face-centred cubic lattice with central forces. (Miss) M. M. Gow (*Proc. Camb. Phil. Soc.*, 1944, 40, 151—166).—The isobars, isotherms, and the dependence of the elastic constns. on temp. are calc., using inverse-power law attractions and repulsions. Results are tabulated for five sets of vals. of the indices in the potential. H. J. W.

Polymorphism of *s*-mono-oleyl-disaturated triglycerides.—See A., 1944, II, 287.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

Magnetic properties of oxygen adsorbed on activated charcoal. C. Courtney (*Compt. rend.*, 1943, 216, 769—771).—The susceptibility, χ , of O_2 adsorbed on C is 107.5×10^6 , which does not differ greatly from the val. for ordinary O_2 . It is possible to determine χ conveniently for a gas by adsorbing it on activated C, since a large mass of gas is conc. into a small vol. A. J. M.

Magnetic properties of hæmatite powders: influence of grain size. R. Chevallier and (Mlle.) S. Mathieu (*Ann. Physique*, 1943, [xi], 18, 258—288).—Magnetisation curves were found with increasing and decreasing fields up to 6500 gauss for samples of uniform microcryst. powders of average grain size d . The coeff. of initial magnetisation falls rapidly with decrease of d , and $\chi \times 10^6$ varies from ~400—500 to 25—30 for grain sizes 300—1 μ . and is ~1750 for very thin films of artificial hæmatite. The true coeff. of magnetisation decreases with increase of field and approaches, for all powder samples, the limiting val. $\chi = 20 \times 10^{-6}$. N. M. B.

Magnetic susceptibility and constitution of nitroso-pentammine cobalt salts. S. P. Ghosh and P. Ray (*J. Indian Chem. Soc.*, 1943, 20, 409—413).—Redetermination of the magnetic moment of the black and red isomerides of $[Co(NH_3)_5(NO)]^{++}$ salts gives a paramagnetic moment of 1.5 Bohr magnetons for the black chloride and a diamagnetic val. for the red nitrate. The electronic structure of the complexes is discussed. L. J. J.

High-temperature heat contents of magnesium nitrate, calcium nitrate, and barium nitrate. C. H. Shomate (*J. Amer. Chem. Soc.*, 1944, 66, 928—929).—High-temp. heat content measurements on $Mg(NO_3)_2$ (399—623° K.), $Ca(NO_3)_2$ (403—815° K.), and $Ba(NO_3)_2$ (411—862° K.) are used to derive equations for heat content and C_p and vals. of entropy (S) for 50° intervals from 350° K. W. R. A.

Melting of crystalline polymers. (Miss) E. M. Frith and R. F. Tuckett (*Trans. Faraday Soc.*, 1944, 40, 251—260).—On the basis of a fringed micelle model a thermodynamic relation is obtained between the m.p. and the proportion θ of amorphous material in the structure. The convergence of m.p. in a homologous series and the existence of a range of melting in materials containing cryst. and amorphous parts in equilibrium are necessary consequences of the theory. Calc. vals. of the cryst.-amorphous equilibrium over a range of temp. agree with experimental data for rubber and polyethylene. Extension of the treatment to stretched polymers is in qual. agreement with observation for rubber. F. L. U.

Dissociation of ammonium chloride. C. C. Stephenson (*J. Chem. Physics*, 1944, 12, 318—319).—The standard free energy of dissociation of NH_4Cl into NH_3 and HCl , calc. from dissociation pressures and heat capacities and from solubility and activity coeffs. of aq. solutions, gives the vals. 21,860 and 21,780 g.-cal. per g. mol., respectively, at 298.1° K., in agreement with the assumption of complete dissociation in the vapour phase. The corresponding vals. for ΔH at 298.1° K. are 42,160 and 42,260 g.-cal. per g.-mol., respectively. The standard entropy of aq. NH_4^+ at 298.1° K. is calc. as 26.5 and 27.1 g.-cal. mol.⁻¹ deg.⁻¹, respectively, from the above sets of data. L. J. J.

Entropy values in homologous series of salt-like solid materials. W. D. Treadwell and B. Mauderli (*Helv. Chim. Acta*, 1944, 27, 567—571).—Comparison of the entropy vals. (S) of various series of elements and compounds indicates that for the corresponding compounds of a group in the periodic classification S increases linearly with the mol. wt. of the compound and can be expressed as $S_{298} = a(\log M_c + \beta \log M_a) + b$, where M_c and M_a are the mol. wts. of the cation and anion, respectively, β = valency of cation/valency of anion, and a and b are const. for the particular series but vary with the series. J. W. S.

Thermal expansion of plastic materials.—See B., 1944, II, 207.

Van der Waals' cohesion constant. F. C. Auluck and R. N. Rai (*Current Sci.*, 1944, 13, 126—127).—Solving the Schrödinger equation for a hole in a liquid leads to expressions for the van der Waals const. $a = 2.4V^2\sigma(\sigma p/h^4)^{1/2}$ and the intrinsic pressure $p_0 = 2.4\sigma(\sigma p/h^4)^{1/2}$ in terms of the mol. vol. V , the surface tension σ , and the density ρ . L. J. J.

Attempt to define a perfect liquid. J. P. E. Duclaux (*Ann. Physique*, 1943, [xi], 18, 209—215).—Theoretical considerations are based on a comparison of the known properties of various liquids in order to determine those of a perfect liquid. N. M. B.

Rheochor and its application. W. V. Bhagwat, P. M. Toshniwal, and V. A. Moghe (*J. Indian Chem. Soc.*, 1944, 21, 29—31).—Vals.

for at. rheochors have been calc., the substitution of $\eta^{\frac{1}{2}}$ for $\gamma^{\frac{1}{2}}$ in the parachor being used (cf. A., 1943, I, 301). The vals. obtained are H 1.77, C 6.44, O 6.02, S 11.28, Cl 11.6, Br 13.8, and Hg 8.75. When substituted for various org. liquids, these vals. reproduce the rheochors of the compounds with fair accuracy; alcohols and aromatic hydrocarbons show marked deviations. The formula $R_m = R(1 - \alpha) + \alpha R_s$, where R_m , R , and R_s are the rheochors of solution, solvent, and solute, respectively, and α is the mol. fraction of the solute in solution, extends the calculation to solutions, e.g., of sucrose. L. S. T.

Viscosity of methyl dilinoleate.—D. W. Young and R. E. Bier-tuempfel (*J. Amer. Chem. Soc.*, 1944, 66, 843—844).—Vals. of η are given for the range -40° to 100° . W. R. A.

Viscosimetric behaviour of malt extracts.—See B., 1944, III, 158.

Thermoplastic flow of polystyrene.—See B., 1944, II, 207.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Molecular state of mixtures. F. Michaud (*Compt. rend.*, 1943, 216, 840—842).—It is shown theoretically that in binary mixtures the relative lowering of v.p. of the two components is the same for that concn. which corresponds to max. free energy, and this is confirmed by vals. taken from "International Critical Tables," which show that the free energy of a binary mixture is a max. when the concns. are equimol. Exceptions occur when the two mols. tend to combine in some ratio other than 1:1. A. J. M.

Diffusion equations, their representation by models, and diffusion experiments with silica gels. III. Diffusion in a defined space with initial local differences of concentration. A. Dobrowsky (*Kolloid Z.*, 1943, 105, 149—160).—The diffusion equations are solved to give the concn. gradients and amounts of substance diffusing after any time, in defined vols. of uniform cross-section, with various boundary conditions. The equations are verified by experiments on the diffusion of aq. $Na_2Cr_2O_7$ in SiO_2 gels, and by hydraulic models (cf. A., 1944, I, 197). J. H. Ba.

Dielectric properties of dipolar ions in mixed solvents. G. Oster (*J. Amer. Chem. Soc.*, 1944, 66, 948—951).—A theory of the decrease in dielectric increment of dipolar ions with decrease in ϵ of the solvent mixture is developed. On the basis of electrostatic theory dipolar ions would be expected to sort out the solvent constituent of higher ϵ , thus producing a shell of material of greater ϵ which would act as an electrostatic shield decreasing the effective dipole moment and dielectric increment of the dipolar ion and becoming more pronounced as the difference in ϵ of the shell surrounding the dipolar ion and that of the liquid in the bulk of the solutions widens. The theory is in general accord with observed results. W. R. A.

Dielectric constants of solutions of glycine and pyridine betaine in water-dioxan mixtures. G. Oster, (Miss) D. Price, L. G. Joyner, and J. G. Kirkwood (*J. Amer. Chem. Soc.*, 1944, 66, 946—948).—Vals. of ϵ for solutions of glycine and pyridine betaine (I) in H_2O -dioxan mixtures at 25° are given. The dielectric increments of both solutes show a regular decrease with decreasing ϵ of the solvent mixture, similar to that exhibited by glycine betaine and the benzbetaines. The possibility of the reversion of (I) to the non-ionised form is examined and calculations have shown that the charged groups could approach each other, and thus account for the experimental results, only if valency bonds were greatly distorted. W. R. A.

Viscosity of aqueous solutions of electrolytes as a function of the concentration. VIII. Potassium ferricyanide. G. Jones and S. M. Christian (*J. Amer. Chem. Soc.*, 1944, 66, 1017—1019).—Data for ρ and η of aq. $K_3Fe(CN)_6$ up to saturation are recorded. Equations connecting ρ , η , and $1/\eta$ with concn. are given. $K_3Fe(CN)_6$ solutions verify the predictions of Falkenhagen and Vernon. W. R. A.

Existence of an intermediate precipitated phase in the decomposition of the solid solution of aluminium and magnesium. P. Lacombe (*Compt. rend.*, 1943, 217, 175—177).—If the Al-Mg system is annealed at a low temp. ($<280^\circ$) and if the re-dissolution of the pptd. phase with rise of temp. is followed by dilatometry or conductivity, there is an anomaly in the curve at 280° . If the duration of annealing is prolonged the anomaly disappears. There is no anomaly if the annealing is carried out at temp. $>280^\circ$. This is due to an intermediate pptd. phase, the occurrence of which has also been followed by X-ray analysis. This indicates that below 280° a phase different from Al_3Mg_2 exists, but if the alloy is heated at $>280^\circ$ for a few min. the pptd. phase disappears and the normal diagram for the β phase is obtained. This result is confirmed by thermal analysis. A. J. M.

Phase diagram of the copper-iron-silicon system from 90 to 100% copper. A. G. H. Andersen and A. W. Kingsbury (*Amer. Inst. Min. Met. Eng., Tech. Publ.* 1510, 1942, 10 pp.; *Metals Tech.*, 9, No. 6).—Cu-Fe and Cu-Fe-Si alloys were examined by the X-ray powder method after quenching from 400—1025°. Fe-rich phases were identified by chemical analysis after removal of the Cu-rich phase with HNO_3 . Isothermal sections of the three-component

diagram are given for temp. between 500° and 875°, and diagrams showing the effect of Si on Cu containing 0.5 and 2% Fe, based on the authors' and previous work. R. K.E.

Rate of precipitation of silicon from solid solution of silicon in aluminium. L. K. Jetter and R. F. Mehl (*Amer. Inst. Min. Met. Eng., Tech. Publ.* 1508, 1942, 16 pp.; *Metals Tech.*, 9, No. 6).—Using a new dilatometer (cf. C., 1944, Part 4) measurements were made for isothermal ageing at temp. of 196–236° for five quenched alloys containing 0.41–1.23% Si. The effect of rate of quenching is also described. The rate of dilation increases with increase in solute concn. and with increasing temp. and also with rate of quenching owing to the nucleating effect of the quenching strain. The results are treated theoretically, assuming that the pptn. is due to formation and growth of nuclei. R. K.E.

Constitution of lead-rich lead-antimony alloys. W. S. Pellini and F. N. Rhines (*Amer. Inst. Min. Met. Eng., Tech. Publ.* 1506, 1942, 7 pp.; *Metals Tech.*, 9, No. 6).—The solidus and eutectic temp. were determined with a specially designed apparatus by observing the temp. at which a slowly heated lightly loaded specimen was ruptured. The solid solubility limit is 3.5% Sb at the eutectic temp., 251.5±0.5°. R. K.E.

Solubility products of copper oxides and hydroxide and the solubility of copper hydroxide in sodium hydroxide solution. W. Feitknecht (*Helv. Chim. Acta*, 1944, 27, 771–775).—The energy of formation of Cu(OH)₂ is recalculated from other thermal data as $\Delta A = -85.41$ kg.-cal. From this and other data the following solubility products (S) are calc. $S_{Cu_2O} = [Cu^{2+}][OH^{-}] = 1.26 \times 10^{-15}$, $S_{CuO} = [Cu^{2+}][OH^{-}]^2 = 1.0 \times 10^{-20}$, $S_{Cu(OH)_2} = [Cu^{2+}][OH^{-}]^2 = 1.6 \times 10^{-19}$. From the Cu remaining in solution immediately after a little Cu(NO₃)₂ is treated with an excess of N-NaOH and the amount remaining after the solution has been kept for 4 months so as to cause pptn. of CuO the equilibrium consts. of the reactions $Cu(OH)_2 + 2OH^{-} \rightleftharpoons Cu(OH)_4^{2-}$, $CuO + H_2O + 2OH^{-} \rightleftharpoons Cu(OH)_4^{2-}$, and $Cu(OH)_2 \rightleftharpoons Cu^{2+} + 4(OH)^{-}$ are calc. as 5.3×10^2 , 6.5×10^3 , and 7.5×10^{-17} , respectively. J. W. S.

Effect of sulphide ion hydrolysis on the solubility-solubility product relationship of metallic sulphides. P. van Rysseberghe and A. H. Gropp (*J. Chem. Educ.*, 1944, 21, 96–99).—A theoretical treatment in which the extensive hydrolysis of S²⁻ is taken into account in establishing the correct relationship between the solubility and the solubility product of sparingly sol. sulphides. The formation of complex ions is the probable explanation of the lack of agreement between simple theory and facts for ZnS, CdS, and CuS. L. S. T.

Mutual solubility in the ternary system cadmium-cobalt-zinc mercurithiocyanates. I. Binary system Cd[Hg(CNS)₂]-Co[Hg(CNS)₂]. M. Straumanis and W. Stahl (*Z. physikal. Chem.*, 1943, A, 193, 97–111).—Co[Hg(CNS)₂] (I), Zn[Hg(CNS)₂] (II), and Cd[Hg(CNS)₂] (III) all crystallise as tetragonal bisphenoidal (S₄), body-centred. The space-group is therefore S₄ with 2 mols. per unit cell. Lattice consts. at room temp. are, respectively: a 11.0868, 11.0616, 11.4403, c 4.3652, 4.4287, 4.2043 Å., c/a 0.3937, 0.4002, 0.3675, v 536.56, 541.90, 550.26 Å.³ The (I)-(II) system shows complete miscibility by exchange between Co₂ and Cd₂ with deformation of the crystal. The Vegard additivity law holds within experimental error. L. J. J.

Solubilities of high mol. wt. symmetrical normal aliphatic tertiary amines. A. W. Ralston, C. W. Hoerr, and P. L. Du Brow (*J. Org. Chem.*, 1944, 9, 259–266).—Solubilities of N(C₆H₁₃)₃ (I), N(C₁₂H₂₅)₃ (II), and N(C₁₅H₃₁)₃ (III) have been determined at 10° intervals between -60° and 60° in C₆H₆, cyclohexane (IV), CCl₄, CHCl₃, Et₂O, EtOAc, BuOAc, COMe, COMeEt, MeOH, 95% EtOH, PrⁿOH, and BuⁿOH. The solubility curves are generally similar to those of the corresponding primary and sec. amines (cf. A., 1944, I, 123; II, 248), from which the tert. amines differ in being more sol. in (IV) than in C₆H₆. (III) differs from all other amines studied in being less sol. in CHCl₃ than in CCl₄ at lower concns. (I), (II), and (III) form simple eutectics with C₆H₆, (IV), and CCl₄. With increase in polarity of the solvent solubility decreases markedly, especially at lower temp., and in several solvents a region of two immiscible solutions appears. H. W.

Solubilities of high mol. wt. normal aliphatic primary alcohols. C. W. Hoerr, H. J. Harwood, and A. W. Ralston (*J. Org. Chem.*, 1944, 9, 267–280).—Solubilities of the alcohols with 10, 12, 14, 16, and 18 C have been determined between -40° and 50° in the solvents used for tert. amines (preceding abstract), and in EtNO₂ and MeCN. The behaviour of the alcohols is similar to that of other long-chain compounds studied, and their solubility curves resemble those of the nitriles and acids (cf. A., 1944, I, 122; 1943, I, 87), which have a similar degree of polarity. Simple eutectics are formed with C₆H₆, cyclohexane, and CCl₄, in which the solubilities decrease in the order given. With increasing polarity of the solvent the solubilities decrease at lower and increase at higher temp. In highly polar solvents two immiscible solutions appear over considerable ranges of concn., as with the tert. amines; an exception to this behaviour is provided by C₁₅H₃₃.OH and C₁₈H₃₇.OH in EtNO₂. With increase in the mol. wt. of the alcohol the solubility curves become steeper

at low and flatter at higher concns. The behaviour cannot be accounted for by mol. association alone. H. W.

Accommodation coefficients on gas-covered platinum. I. Amdur, M. M. Jones, and H. Pearlman (*J. Chem. Physics*, 1944, 12, 159–166).—At room temp., accommodation coeffs. (a) on a completely gas-covered Pt wire are: He 0.403±0.001, Ne 0.700±0.002, Ar 0.847±0.002, Kr 0.844±0.002, Xe 0.858±0.002, H₂ 0.312±0.001, D₂ 0.393±0.001, N₂ 0.769±0.002, CO 0.772±0.002, O₂ 0.782±0.002. Temp. is without influence at 18.9–30.5°. a increases with pressure up to ~0.1 mm. and then remains const. throughout the range of free mol. conduction. Results are corr. for radiation, wire conduction, and free mol. conduction effects on temp. distribution along the Pirani gauge wire used. L. J. J.

Adsorption analysis. I. A. Tiselius (*Kolloid-Z.*, 1943, 105, 101–109).—When a solution is passed through an adsorbent, e.g., activated charcoal, the solute is adsorbed so that pure solvent passes until the adsorbent is saturated with solute, after which the solution appears separated by a sharp boundary from the solvent. In a solution having several solutes, several boundaries are obtained. In the apparatus described an interferometer is used for observing these boundaries and three methods of application are described. In "front" analysis the vol. of solvent passed before the appearance of the solution front (retardation vol., v_r) is measured. v_r (when corr. for solvent initially present on the adsorbent) is equal to the adsorption coeff. α_A at the concn. used, and the method can be applied in certain cases to the determination of adsorption isotherms. Retardation vols. are given for various sugars (in 0.2% aq. solution), amino-acids, and peptides (in 0.5% aq. solution). In the case of mixed solutes mutual influence on the vals. of α_A is observed unless the individual α_A are widely different. This interference occurs in a mixture of lauric and palmitic acids. In elution analysis the adsorbed solute is washed through by a solvent, which produces zones of the solutions travelling with speeds dependent on α_A. Zone spreading introduces difficulties, but the method gives useful results when the solute is weakly adsorbed. In displacement analysis the adsorbed solute is displaced by another solute (e.g., PhOH), in which case the zones are usually well defined. A separation of such similar substances as sucrose and maltose is observed by this method. Difficulties arise with very weakly adsorbed solutes (zone spreading) and displacement is not usually quant., but it can be made so by preliminary treatment of the adsorbent. J. H. BA.

Water sorption by maize starch.—See B., 1944, III, 157.

Elucidation of dyeing processes. R. Haller (*Kolloid-Z.*, 1943, 105, 47–149).—Consideration of the data on the dyeing of Al₂O₃ (produced by anodic oxidation or suspended in H₂O) shows that the dyeing efficiency depends on the degree of dispersion of the Al₂O₃ and of the dye. Even if the dyeing process is a chemical reaction, as for certain animal fibres, it may in certain conditions be based on adsorption. J. H. BA.

Surface of solids. X. Extension of the attractive energy of a solid into an adjacent liquid or film, the decrease of energy with distance, and the thickness of the film. W. D. Harkins and G. Jura (*J. Amer. Chem. Soc.*, 1944, 66, 919–927).—Practically every film adsorbed on the surface of non-porous solids has been found to be highly multimol. at v.p. slightly < saturation. The effect of distance on the intermol. attraction between a solid and an adjacent liquid or an adsorbed layer has been determined in energy units. The energy decays exponentially with distance. The energy of vaporisation of H₂O at 25° (Q) is 10,540 g.-cal. per mol., but if the water is adsorbed on a clean surface of cryst. TiO₂ (anatase) this energy is increased by amounts depending on the no. of layers of H₂O adsorbed, the vals. for one, two, three, four, and five layers being 6550, 1380, 450, 80, and 40 g.-cal. per mol. > Q. Consequently at least 5 mol. layers of H₂O should be adsorbed on anatase before saturation of the vapour is attained and experimental evidence shows thicknesses of >15 Å. With N₂ at -195.6° the measured thickness is 36 Å. (10 mol. layers). At 0° n-C₄H₁₀ attains a thickness of 64 Å., but the thickness of the first mol. layer is ~4 Å. since the mols. lie flat on the surface. Until about the seventh layer the degree of orientation is small but thereafter the surface of the film should exhibit practically the same orientation as liquid n-C₄H₁₀. These results are not in accord with Langmuir's theory of unimol. layers, or with the combined monolayer plus capillary condensation theory. They show that films adsorbed on plane surfaces usually attain greater thicknesses than on porous solids, but PrⁿOH on BaSO₄ is an exception and H₂O on hydrophobic solids should also be an exception. Whilst these results show general agreement with the multimol. theory of Brunauer, Emmett, and Teller (A., 1938, I, 190), the assumption in the theory that the energy of vaporisation of the second adsorbed layer is > the energy of vaporisation of the liquid is shown to be incorrect. Capillary condensation does not appear to play an important role in the sorption with cryst. powders of the type used. W. R. A.

Surface tension and van der Waals' equation. F. C. Auluck and R. N. Rai (*J. Chem. Physics*, 1944, 12, 321–322).—Fürth's "hole"

treatment of liquids (A., 1941, I, 369) leads to a connexion between the van der Waals const. a and the surface tension (γ). The treatment gives the relation $a = 1.3V^2[\gamma^{3/2}/(kT)^{1/2}]$. Vals. calc. for a no. of liquids differ from the corresponding vals. of a from gas data by a nearly const. factor of ~ 2 . A similar degree of agreement is given by vals. of a calc. from γ and ρ vals. by means of the Schrodinger equation. L. J. J.

Pseudo-optics in capillary phenomena. II. R. E. Liesegang (*Kolloid-Z.*, 1943, 105, 98—101; cf. A., 1944, I, 58).—The method of analysis of mixtures by means of capillary rise on unglazed paper is extended by applying it to small drops of mixture solution previously dried on the paper, and allowing the capillary rise of H_2O to take place first in one direction, followed by drying, and then in the direction at right angles. Pseudo-optical effects produced by pore blocking and cuts in the paper tend to obscure the resulting picture, but any confusion can be overcome by marking the water line at intervals. J. H. Ba.

Structure of the collodion membrane and its electrical behaviour. VIII. Quantitative studies concerning the acidic properties of collodion and their correlation with membrane structure and activity. K. Sollner and J. Anderman. **IX.** Water uptake and swelling of collodion membranes in aqueous solutions of organic electrolytes and non-electrolytes. K. Sollner and P. W. Beck (*J. Gen. Physiol.*, 1944, 27, 433—449, 451—460).—VIII. A no. of collodion (I) preps. were brought into the state of free acids by exchange of all other cations for H^+ and their acid nos. in the dissolved state and their base-exchange capacities in the fibrous state were determined. The acid no. is lowest for highly purified (I) and highest for highly oxidised (I), but the ratio of the extremes of acid nos. is only 1:3.3, corresponding with a mean equiv. wt. ratio of 100,000:30,000. Base-exchange capacities vary considerably, the ratio of the lowest and highest vals. being 1:200. In electrochemically inactive (I) only one in 770 acid groups is available for base exchange, whereas in the most active (I) one group in 13 is available. The high vals. obtained for oxidised (I) are due not so much to the high acid nos. as to their more open micellar structure. This structural difference is ascribed to the presence of a small fraction of low mol. wt. which inhibits normal formation and arrangement of micelles. There is reasonably good correlation between acid no. and electrochemical activity, low acid nos. being found with the least active preps., but correlation between base-exchange capacity and activity is poor, low capacity vals. being accompanied by low as well as high activity, although high capacities are always associated with high activities.

IX. The swelling of dried (I) in aq. solutions of org. electrolytes and non-electrolytes depends on the nature of the solute. No significant swelling occurs with hydrophilic solutes, e.g., EtOH, $PhSO_3H$, $2-C_{10}H_7SO_3H$, glycerol, glucose, citric acid, but with carbophilic solutes, e.g., higher alcohols and fatty acids, where swelling effect increases with increasing mol. wt., $PhOH$, $m-NO_2-C_6H_4OH$, the swelling is $>$ in absence of solute. The amount of H_2O taken up by (I) in presence of some solutes is the amount taken up in absence of solute; (I) which has thus accumulated a significant quantity of org. solute has probably a different structure from (I) wetted with H_2O only. C. R. H.

Diffusion of gaseous hydrocarbons through rubber membranes. L. Long (*J. Chem. Educ.*, 1944, 21, 139—141).—Apparatus, method, and results for diffusions of C_7H_{16} and of $iso-C_8H_{18}$ through various diaphragms of rubber and neoprene under different conditions of temp. and pressure are described. L. S. T.

Effects of pressure on the properties of liquids and solutions of electrolytes. B. B. Owen (*J. Chem. Educ.*, 1944, 21, 59—63, 84; cf. A., 1943, I, 298).—The dependence on pressure of the partial molal vols. of the components of ionic reactions is discussed, and a correlation of their behaviour in terms of ionic dimensions is attempted, the equations of Tait and of Born and Tammann's hypothesis being used for the purpose. A relationship between ϵ and sp. vol. of the pure solvent is derived. L. S. T.

Magnetic rotativities. III. Ionic (heteropolar) associations. R. de Malleman (*Ann. Physique*, 1943, [xi], 18, 56—72; cf. *ibid.*, 1942, [xi], 17, 360).—A theoretical examination of rules for mixtures, and electrolyte solutions. Conclusions based on considerations of available data are discussed. N. M. B.

Effect of the colloidal state or suspensions on the transmission of infra-red up to 20,000 Å. through substances. M. Deribere (*Compt. rend.*, 1943, 217, 201—211).—The transmission of infra-red rays by a suspension of bentonite has been studied. Thin sheets of bentonite were also prepared. The leaflets transmitted infra-red radiation much better than the suspensions. The Brownian movement thus affects the transmission considerably. A. J. M.

Structure of highly purified sulphide sols. III. Structure and temporary reactions of highly purified sulphur sol. W. Pauli, E. Russer, and P. Balog (*Helv. Chim. Acta*, 1944, 27, 585—612; cf. A., 1937, I, 237, 514).—S sol. prepared by interaction of conc. H_2SO_4 and conc. aq. $Na_2S_2O_3$ pptn. with saturated aq. NaCl and agitation of the ppt. with H_2O , followed by electro-dialysis, is yellow by reflected and orange yellow by transmitted light. The $[H^+]$

calc. from the conductivity of the sol is $<$ that determined by conductometric titration with NaOH or $Ba(OH)_2$ but increases gradually when the sol is kept. From the Ag^+ consumed and H^+ liberated when the sol is treated with $AgNO_3$ and immediately titrated with NaOH the amounts of $H_2S_2O_3$ and polythionic acids (I) present have been determined. Results on a coagulum obtained by freezing the sol indicate that the $H_2S_2O_3$ is firmly bound to the S, whilst (I) is an impurity in the aq. phase. The sol gradually reacts directly with $AgNO_3$, I, and NaOH and the reactions involved are discussed. The case of coagulation by electrolytes follows the normal order of cations and anions, excepting that increase in $[H^+]$ has a stabilising effect. The markedly hydrophilic character of the sol is accounted for by the high proportion of stabilising electrolyte, ~ 1 mol. of $H_2S_2O_3$ to 4 atoms of S. J. W. S.

Variation of magnetic properties of ferric hydroxide sols on addition of hydrochloric acid. A. Boutaric and (Mlle.) P. Berthier (*Compt. rend.*, 1943, 216, 757—758).—Making use of the law of addition of magnetic properties it is possible to obtain the susceptibility (χ) of $Fe(OH)_3$ sols, and its variation with the addition of various amounts of HCl (0.05—0.5N). χ increases with $[HCl]$, and with time, approaching the limiting val. $+193 \times 10^{-6}$. This is of the same order as χ for Fe^{III} salts in solution. The method makes it possible to follow the progressive breakdown of micelles of $Fe(OH)_3$. A. J. M.

Precipitation of proteins by synthetic detergents. F. W. Putnam and H. Neurath (*J. Amer. Chem. Soc.*, 1944, 66, 692—697).—Anionic detergents ppt. proteins only in the cationic form, no pptn. occurring at pH $>$ the isoelectric point of the protein. In the system cryst. horse serum-albumin-Na dodecyl sulphate pptn. is related to protein-detergent wt.-conc. ratio, pH, temp., and ionic strength. When protein-detergent complexes are dissociated by Ba salts the recovered protein is in a regenerated state, as indicated by diffusion, viscosity, and electrophoresis studies. The mechanism and applications of the methods are discussed. W. R. A.

Effect of polyhydric alcohols on the solubilisation of proteins in an organic medium. J. Loiseleur (*Compt. rend.*, 1943, 216, 904—905).—The addition of $(CH_3OH)_n$, like that of the aliphatic acids, aids dissolution of proteins in org. solvents (A., 1931, 166). Unlike the acids, polyhydric alcohols do not greatly assist the direct dissolution of dry proteins, but when added to an aq. solution of a protein they prevent its pptn. by EtOH, $COMe_2$, CCl_3CO_2H , $OH\cdot C_6H_4(NO_2)_3$, etc. Dilution of these "protected" solutions with H_2O causes immediate pptn. of the protein. The dielectric const. of the protein solution is considerably decreased by the addition of the polyhydric alcohol. This affects the dissociation of the protein, favouring formation of the zwitterion. This fact alone is insufficient to explain the phenomenon, but there may be some physical association of the polyhydric alcohol with the protein. A. J. M.

VI.—KINETIC THEORY. THERMODYNAMICS.

Strength of strong acids. J. V. Chodakov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 117—119).—The author's semi-empirical formula for the dissociation const. of an acid in terms of its anionic radius r (in crystals) is $1.32/r \propto 0.84 - 0.042 \log k$, giving $k = 10^8$ for H_2SO_4 and 10^5 for HCl. Evidence supporting a higher strength for H_2SO_4 than for HCl is reviewed. L. J. J.

Effect of substituents on the dissociation constants of carboxylic acids. J. N. Sarmousakis (*J. Chem. Physics*, 1944, 12, 277—288).—Vals. of $\log K_{A_{H_2O}}$, the ratio of dissociation const. of a substituted acid to that of the parent acid, are calc. for p - and m -substituted benzoic acids, by means of the Kirkwood-Westheimer theory on the basis of an oblate spheroidal mol. model. Agreement with experimental vals. is good for the m -acids, but the p -acids show differences which are ascribed to resonance affects. The differences vary very little with the single-component hydroxylic solvent used. L. J. J.

Ionisation constants of very weak acids. Acetoxime, methyl ethyl and diethyl ketoximes. C. V. King and A. P. Marion (*J. Amer. Chem. Soc.*, 1944, 66, 977—980).—The rate of decomp. of nitroso-triacetonamine, catalysed by OH^+ , has been measured as a function of ionic strength (μ) at 24.9° up to $[OH^+] = 0.05$ and $\mu = 0.22$ and may be expressed as $k = (1.209 - 0.479 \mu)[OH^+]$. The acid dissociation consts. of the ketoximes have been determined as a function of μ , using the catalytic reaction above to measure the $[OH^+]$ of NaOH partly neutralised by ketoxime. W. R. A.

Steric strain and the anomalous base strength of normal aliphatic amines. H. C. Brown and M. D. Taylor (*J. Amer. Chem. Soc.*, 1944, 66, 846—847).—The base strength of n -aliphatic amines referred to BMe_3 as standard acid increases from NH_3 to NH_2Me , decreases with NH_2Et , and then increases regularly, thus displaying a very close similarity to n -aliphatic acids. It is suggested that this behaviour results from steric interference, and that the point in the series at which weakening is exhibited will depend on the size of the mol. of the reference acid; the larger is the acid the earlier in the series will weakening be shown. W. R. A.

Effect of sodium chloride on the pH of *p*-phenolsulphonate buffers from 9° to 80°. R. G. Bates and S. F. Acree (*J. Res. Nat. Bur. Stand.*, 1944, 32, 131—143).—E.m.f. measurements on mixtures of $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{K}$, NaOH, and NaCl have been made over the range 0—60°. For a given composition pH decreases with temp., and for a given temp. pH decreases with increase in [NaCl]. The effect of NaCl on pH is satisfactorily accounted for solely by the change in ionic strength and activity coeffs. on addition of a third ionised component to the buffer. Abnormal and sp. effects due to Na^+ and Cl^- appear to be absent. Equations permitting the calculation of the effect of NaCl on pH are given. A method for the calculation of the ionic strength and pH of unknown mixtures of sulphonate and NaOH by determining the e.m.f. in presence of two different concns. of NaCl has been devised. C. R. H.

Thermodynamics of azeotropic solutions. I. Shift of equilibrium in binary systems. O. Redlich and P. W. Schutz (*J. Amer. Chem. Soc.*, 1944, 66, 1007—1011).—Since the azeotropic equilibrium of a solution of two miscible liquids is characterised by three intensive variables (temp., pressure, and composition), the shift in equilibrium is exhaustively described by two relations between the variables. Assuming that the vapour is a perfect gas mixture two expressions have been derived, in which relations between the variables are given in terms of ascertainable thermodynamic quantities. Azeotropic temp.—composition curves depend on whether one or both components are normal, dissociating, or associating. Dil. azeotropic solutions of a dissociating substance belong to the min. v.p. type. Only when a dissociating component is present does the temp.—composition curve increase or decrease without limit with decreasing concn. in dil. solutions. When the temp.—composition curve of a max. (min.) v.p. system extends to a pure component, this component is the more (less) volatile member. This rule holds for both upper and lower limits of the azeotropic temp. range. "Isobaric temp." is suggested for the temp. at which the v.p. of the pure components are equal. The slope of the temp.—composition curve is steep at this temp. if both components exhibit only small deviations from Trouton's rule. W. R. A.

System acetic acid—ammonia. A. W. Davidson, H. H. Sisler, and R. Stoenner (*J. Amer. Chem. Soc.*, 1944, 66, 779—782).—The temp.—concn. curve of the system $\text{AcOH}\cdot\text{NH}_3$ has been extended (cf. A., 1930, 406) to 100 mol.-% NH_3 . The m.p. of NH_4OAc is 117°. Solid compounds, $5\text{NH}_3\cdot 4\text{AcOH}$, $9\text{NH}_3\cdot \text{AcOH}$, and (probably) $2\text{NH}_3\cdot \text{AcOH}$ have been shown to exist. Comparison with the $\text{H}_2\text{O}\cdot\text{NH}_3$ system is made. W. R. A.

System sulphur dioxide—acetic acid. W. H. Scheub and C. R. McCrosky (*J. Amer. Chem. Soc.*, 1944, 66, 841).—The m.p. curve shows the existence of the compound $\text{SO}_2\cdot \text{AcOH}$ (m.p. -38°). The eutectic points are -46.1° and -80.3°, corresponding with 13.2 and 78.4 mol.-% SO_2 . W. R. A.

Binary systems formed from nitriles and halides of titanium, tin, and antimony.—See A., 1944, II, 250.

Binary system tin tetrachloride *m*-dinitrobenzene.—See A., 1944, II, 253.

Ternary system silver bromate—sodium bromate—water. J. E. Ricci and J. J. Aleshnick (*J. Amer. Chem. Soc.*, 1944, 66, 980—983).—The system $\text{AgBrO}_3\text{—NaBrO}_3\text{—H}_2\text{O}$ has been investigated at 25° and partly studied at 0° and 50°. The compound $\text{AgBrO}_3\cdot \text{NaBrO}_3$ (I) is formed. (I) forms a continuous solid solution with AgBrO_3 . NaBrO_3 forms a solid solution containing up to 3.0% AgBrO_3 . Ppts. of AgBrO_3 formed in the presence of Na^+ and excess of BrO_3^- ions must be contaminated with NaBrO_3 ; this would explain the difficulty of obtaining AgBrO_3 of const. solubility. The effect of these results on analytical procedures is discussed. The solubility of AgBrO_3 at 25° is 0.204%. W. R. A.

Ternary system barium bromate—barium chlorate—water at 25°. J. E. Ricci and S. H. Smiley (*J. Amer. Chem. Soc.*, 1944, 66, 1011—1016).—From solubility equilibrium relations at 25° of the system $\text{Ba}(\text{BrO}_3)_2\text{—Ba}(\text{ClO}_3)_2\text{—H}_2\text{O}$ the formation of a continuous solid solution of $\text{Ba}(\text{BrO}_3)_2\cdot \text{H}_2\text{O}\text{—Ba}(\text{ClO}_3)_2\cdot \text{H}_2\text{O}$ is shown and this would explain why it is difficult to determine BrO_3^- in the presence of ClO_3^- by addition of a Ba salt. The system shows positive deviations from ideality (type II of Roozeboom's classification of solid solutions). The distribution const. for the two salts between their aq. solutions and the saturating solid solution was found to be $\log K = 2.0$, in fair agreement with the val. calc. from aq. solubilities of the salts, $\log K = 1.8$. The discrepancy is considered to result from the uncertainty regarding the val. of the activity coeff. of $\text{Ba}(\text{ClO}_3)_2$. W. R. A.

Systems $\text{NaClO}_3\text{—NaBr}\cdot\text{H}_2\text{O}$, $\text{NaClO}_3\text{—NaI}\cdot\text{H}_2\text{O}$, and $\text{NaClO}_3\text{—NaNO}_3\cdot\text{H}_2\text{O}$ at 25°. J. E. Ricci (*J. Amer. Chem. Soc.*, 1944, 66, 1015—1016).—Solubility measurements on the systems $\text{NaClO}_3\text{—NaBr}\cdot\text{H}_2\text{O}$, $\text{NaClO}_3\text{—NaI}\cdot\text{H}_2\text{O}$, and $\text{NaClO}_3\text{—NaNO}_3\cdot\text{H}_2\text{O}$ at 25° indicate that these salt pairs do not form double salts or solid solutions at this temp. W. R. A.

Heat of formation of solid and liquid $\text{Mn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$. C. H. Shomate and F. E. Young (*J. Amer. Chem. Soc.*, 1944, 66, 771—

773).—By measuring the heats of dissolution in $n\text{-H}_2\text{SO}_4$ at room temp. the heats of formation of $\text{Mn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ have been determined as (liquid) $-557,070 \pm 310$, (solid) $-566,680 \pm 310$ g.-cal. per g.-mol. The heat of fusion is 9610 ± 10 g.-cal. per g.-mol. W. R. A.

Heats of formation of $\text{Mg}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, and $\text{Ba}(\text{NO}_3)_2$. F. E. Young (*J. Amer. Chem. Soc.*, 1944, 66, 773—777).—From measurements of heats of dissolution in $n\text{-HCl}$ the heats of formation at 25° are calc.: $\text{Mg}(\text{NO}_3)_2$ -188,770 \pm 310; $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ -624,410 \pm 310; $\text{Ca}(\text{NO}_3)_2$ -224,050 \pm 360; $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ -509,420 \pm 370; $\text{Ba}(\text{NO}_3)_2$ -236,990 \pm 380 g.-cal. per mol. W. R. A.

Heats of formation of $\text{Al}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$. F. E. Young (*J. Amer. Chem. Soc.*, 1944, 66, 777—779).—From measurement of the heats of dissolution of the nitrates and of Al in 4*n*-HCl the heats of formation at 25° are: $\text{Al}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ -680,890 \pm 460 and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ -897,590 \pm 470 g.-cal. per g.-mol. W. R. A.

VII.—ELECTROCHEMISTRY.

Redox potential of ferric solutions practically free from ferrous ions. (Mlle.) D. Bezzer (*Compt. rend.*, 1943, 216, 798—800).—The usual expression for the redox potential of a system, obtained by considering that both oxidised and reduced ions are present in considerable quantities, fails when applied to a solution containing only one type of ion. The potential curves as a function of pH have been obtained for solutions of $\text{Fe}(\text{ClO}_4)_3$ containing 10^{-1} to 10^{-4} g.-ion of Fe per l. For a given solution at different pH vals. the potential is const. so long as $[\text{Fe}^{3+}]$ is const. It decreases when $\text{Fe}(\text{OH})_3$ is pptd. In the region where the potential is const. it is given by $E - E_0 + 0.06 \log [\text{Fe}^{3+}]$. The method used shows at what pH vals. $\text{Fe}(\text{OH})_3$ is pptd. At the pH at which pptn. commences all the Fe is in the form of Fe^{3+} and not $(\text{FeOH})^+$ or $(\text{FeO})^+$. The method also gives information concerning the formation of complexes by Fe^{3+} . A. J. M.

Progressive decrease of current during electrolysis of acids and bases. P. Jolibois (*Compt. rend.*, 1943, 217, 133—134).—When a strong acid or a strong base is electrolysed in a U-tube at const. p.d., the current progressively decreases until it is practically zero. This cannot be explained as due to polarisation, but an adequate explanation is given on the author's view of cataphoresis involving hydrated ions (A., 1944, I, 176, 178), according to which the acid becomes more conc. at the anode, whilst the cathode becomes surrounded with H_2O , the extent depending on time. In the case of a salt, e.g., K_2SO_4 , the current increases with time, as the electrolytes around the electrodes become H_2SO_4 and KOH , which conduct better than the original solution. A. J. M.

Anodic passification of copper in dilute sodium hydroxide solution. W. Feitknecht and H. W. Lenel (*Helv. Chim. Acta*, 1944, 27, 775—789).—The c.d.—voltage and c.d.—time curves for Cu electrodes in 0.01—1*N*-NaOH show the usual course of anode processes leading to passification. The anodic films produced on the Cu have been examined by microscopic and X-ray methods. If the electrolyte is stirred during passage of the current a film of Cu_2O is first formed and this gradually passes into CuO . If this transition is completed a sudden rise in potential occurs at const c.d. If the electrolyte is not stirred a film of $\text{Cu}(\text{OH})_2$ is formed over the Cu_2O . The thickness and structure of the surface film depend on the orientation of the crystallites. The possible anodic reactions are discussed. J. W. S.

Polarographic examination of carbonyl compounds. J. M. Lupton and C. C. Lynch (*J. Amer. Chem. Soc.*, 1944, 66, 897—900).—Reduction of aldehydes and ketones in acid N_2H_4 solutions has been carried out polarographically with Pr^+CHO , COMe_2 , $\text{COMe}\cdot\text{CH}_2\text{Bu}^+$, and COMeBu^+ from 0.0001 to 0.01*M*. Equations relating diffusion current and concn. are given. The precision is between 2 and 5%. W. R. A.

VIII.—REACTIONS.

Flammability limits in air [of] methyl chloride and its mixtures with dichlorodifluoromethane. K. S. Willson and W. O. Walker (*Ind. Eng. Chem.*, 1944, 36, 466—468).— MeCl -air mixtures are flammable in the range 7.6—19.1% (v/v) of MeCl , but ignition does not occur in presence of $<10\%$ (v/v) of CCl_2F_2 . $\text{MeCl}\text{—CCl}_2\text{F}_2$ mixtures containing $>35\text{—}0\%$ (w/w) of MeCl are non-flammable in air. The above vals. were obtained with a 15,000-v. spark, which gave the widest flammability range and is concluded to be the most reliable method. Igniting matches gave similar results, but low-voltage sparks gave ignition only within narrow limits, and ignition by flame was very variable. Ignition could not be obtained by red-hot wire or burning cigarette. M. H. M. A.

Influence of *n*-alkyl groups on the rate of a cyclisation reaction.—See A., 1944, II, 254.

Reaction of dibromides of mono-substituted ethylenes with potassium iodide. D. Pressman and W. G. Young (*J. Amer. Chem. Soc.*, 1944, 66, 705—709).—Reaction rate coeffs. and heats and

entropy of reaction have been determined for the reaction between KI and $\text{CH}_3\text{RBr}\cdot\text{CH}_2\text{Br}$ ($\text{R} = \text{Pr, Ph, CH}_2\text{Ph, CH}_2\text{OH, CO}_2\text{H, Br}$) in 99% MeOH. Both Br atoms can react and do so with different rates and different heats of activation. Thus no significance may be attached to the effect of various substituents on the observed vals. W. R. A.

Relations between chemical activity and absorption in the ultra-violet of certain organic molecules. X. Velocity of hydrolysis of substituted amides of acetoacetic acid. XI. Velocity of replacement of chlorine atoms in the chloro-derivatives of the substituted amides of acetoacetic acid. R. K. Trivedi and B. N. Mankad (*J. Indian Chem. Soc.*, 1943, 20, 415–420, 421–423).—X. The relative rates of hydrolysis in acid and alkaline solutions of the anilide, *o*- and *p*-tolylamide, α - and β -naphthylamide, and *m*-4-xylylamide of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ show a parallel effect of substitution on absorption spectrum and chemical reactivity; they indicate that reactivity is affected by the nature of the radicals attached to the $\cdot\text{NH}\cdot$ group, and is enhanced by asymmetry of the mol.

XI. The velocity of replacement of Cl by H in the compounds referred to in Part VIII (A., 1944, I, 211) increases with the asymmetry of the mol., in the order anilide < *m*-4-xylylamide < α -naphthylamide. L. J. J.

Hydrolysis of trimethylethylene dibromide. Mechanism of ketone formation.—See A., 1944, II, 285.

Acetylenic ethers. IV. Hydration.—See A., 1944, II, 287.

Kinetics of polymerisation reactions. G. Gee and H. W. Melville (*Trans. Faraday Soc.*, 1944, 40, 240–251).—A general treatment of polymerisation kinetics is given for the extreme conditions where the half-life of the monomer is and the lifetime of chain growth, when the velocity coeffs. of propagation are independent of mol. size, and in the second case when they depend on mol. size. Size distributions are computed where possible. F. L. U.

Degradation of long-chain molecules. I. H. H. G. Jellinek (*Trans. Faraday Soc.*, 1944, 40, 266–273).—The thermal degradation of polystyrene at $\sim 300^\circ$ in a vac. stops or slows down markedly when a certain chain length is reached, and the size distribution curve for the products is narrower than is predicted by the theory which assumes that each link is equally strong and equally accessible. The degradation of chains having equal nos. of weak links distributed at random is investigated theoretically, and the no. and wt. distribution functions, and the wt.-average chain lengths, are calc. In practice the condition that only weak links are ruptured will not usually be strictly fulfilled, and the required distribution functions must be obtained by combining the "weak link" theory with that dealing with chains having no weak links. F. L. U.

Study of the mechanism of polymerisation reactions by means of size distribution curves. E. F. G. Herington (*Trans. Faraday Soc.*, 1944, 40, 236–240).—The interpretation of size distribution curves is considered for polymerisations in which the mean life of active chain centres is very small compared with the half-life of the total reaction. If the degree of polymerisation is known and its extent small ($>10\%$ polymerised) information about the mechanism terminating the life of an active radical may be obtained from the form of the distribution curve. Three main types of curve are distinguished and discussed. Experimental complications often arise and the chief of these are indicated. F. L. U.

Nitration of cellulose. I.—See A., 1944, I, 174.

Induced oxidation of oxalic acid by dichromate with ferrous sulphate as inductor. C. R. Viswanadham and G. G. Rao (*Current Sci.*, 1943, 12, 327).—Oxalates interfere with the titration of FeSO_4 by dichromates. This is due to induction of the reaction between $\text{C}_2\text{O}_4^{2-}$ and $\text{Cr}_2\text{O}_7^{2-}$ by the rapid reaction of FeSO_4 with $\text{Cr}_2\text{O}_7^{2-}$. FeSO_4 also induces the reaction between $\text{Cr}_2\text{O}_7^{2-}$ and tartaric, citric, and malic acids, but not succinic acid. J. O'M.B.

Effect of dielectric constant and temperature on the catalysed decomposition of azodicarbonates ion. C. V. King and J. J. Josephs (*J. Amer. Chem. Soc.*, 1944, 66, 767–771).—The rate of decomp. of the $\text{N}_2(\text{CO}_2)_2^{+}$ ion at five temp. from 15° to 35° in dil. aq. NaOH and in dil. aq. NaOH + dioxan (up to 60%) is determined. Molar H^+ catalysis const. at zero ionic strength, calc. from rates, vary with ϵ of the medium, in satisfactory agreement with theoretical predictions. Temp. coeffs., energies and entropies of activation have been calc. and agree with those calc. by the Eyring "absolute rate" and collision rate theories. W. R. A.

Mechanism of peroxide-initiated styrene polymerisation. H. F. Pfann, D. J. Salley, and H. Mark (*J. Amer. Chem. Soc.*, 1944, 66, 983–985).—The Br content in polymers obtained from liquid styrene and (*p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{O}$)₂ at various temp. has been determined gravimetrically and with the aid of Br^+ . Vals. from the two methods agree and indicate between 1 and 3 Br atoms per chain. W. R. A.

Catalysis of the interaction between hydrogen sulphide and sulphur dioxide by silver sulphide. B. S. Rao (*Current Sci.*, 1943, 12, 323).—The reaction of H_2S and SO_2 is autocatalytic in presence of Ag owing to the formation of Ag_2S , the activity of which \propto the v.p.

of H_2O in the system. The kinetics of the reaction can be examined in a glass apparatus if the v.p. is kept sufficiently low by means of an appropriate hygostat. J. O'M.B.

Catalytic activity of silver sulphide. B. S. Rao and M. R. A. Rao (*Current Sci.*, 1943, 12, 323).— Ag_2S catalyses the decomp. of SO and its polymer, S_2O_8 . The reaction between H_2S and SO is catalysed in absence of H_2O (cf. preceding abstract). J. O'M.B.

Redistribution reactions in the halides of carbon, silicon, germanium, and tin. G. S. Forbes and H. H. Anderson (*J. Amer. Chem. Soc.*, 1944, 66, 931–933).—With slightly moistened AlCl_3 as catalyst, mixtures of CCl_4 and CBr_4 , as well as CCl_3Br and CCl_2Br_2 , rearrange at 170° for 7 hr. until halogen atoms are distributed among the five members of the series according to the laws of probability. Corresponding rearrangements of Si chloro-bromides and -iodides without a catalyst are partial in 70 hr. at 140° but complete and rapid after passage through a tube at 600° . These random mixtures can be fully separated by fractional distillation at normal pressure without appreciable rearrangement. Distillation curves of the hot tube product from GeCl_4 and GeBr_4 indicate the likely existence of GeCl_3Br (b.p. $\sim 112^\circ$). Rapid redistribution takes place on redistillation of such a fraction. No irregularities are shown in the shape of the distillation curve of the Sn^{IV} chlorobromides near the b.p. calc. for the mixed compounds. The individual compounds could not be isolated, presumably because of redistribution during distillation, but some indication of redistribution was obtained. None of the phenomena observed was inconsistent with the hypothesis that all the chlorobromides of Ge and Sn^{IV} coexist in random distribution. The stability of the chlorobromides against rearrangement decreases steadily from C to Sn. W. R. A.

Mutual effect of gas flow, diffusion, and chemical reaction in heterogeneous catalysis. C. Wagner (*Z. physikal. Chem.*, 1943, A, 193, 1–15).—For the case of a reacting gas mixture flowing through a bed of compact, porous catalyst granules, differences in gas concn. between the interior and the exterior of the granules can be calc. from experimental data with the aid of the relations formulated by Damkohler, Thiele, and Zeldovitch. Such differences are negligible in laboratory conditions, but are considerable in NH_3 synthesis, where diffusion into the catalyst grains is slight. With appreciable diffusion of N atoms, NH and NH_2 radicles, concn. differences may be negligible for granules of diameter >1 cm. L. J. J.

Excess temperature in catalyst grains. G. Damkohler (*Z. physikal. Chem.*, 1943, A, 193, 16–28).—The max. attainable excess temp. in a stationary catalyst granule is independent of the reaction velocity and the radius of the granule, and dependent only on the heat of reaction, the internal diffusion coeff., the internal thermal conductivity, and the exterior concn. of the reactants. Max. chemical utilisation of the interior of the granule is obtained when the interior excess temp. is a min. Vals. for max. excess temp. are calc. as 0.42° , 0.20° , 0.57° , 1.0° , and 3.0° for $\text{SO}_2 + \frac{1}{2}\text{O}_2$ at 1 atm. on V_2O_5 with ceramic support, $\text{N}_2 + 3\text{H}_2$ at 200 and 1000 atm. on $\text{Fe-Al}_2\text{O}_3\text{-K}_2\text{O}$, $\text{CO} + 2\text{H}_2 \rightarrow \text{MeOH}$ at 240 atm. on ZnO, and $4\text{CO} + 9\text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + 4\text{H}_2\text{O}$ at 1 atm. on Fe-Co-ThO_2 , at 500° , 500° , 400° , and 304° , respectively. L. J. J.

Catalytic formation of methane from carbon monoxide and hydrogen. Nickel and nickel-alumina catalysts prepared from the hydroxide using potassium, sodium, and ammonium hydroxide as precipitants. K. M. Chakravarty and J. M. Sarker (*Current Sci.*, 1944, 13, 127).—Addition of $>0.16\%$ of Al_2O_3 to a Ni catalyst increased the rate of the reaction $2\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2$ relatively to that of $\text{CO} + \text{H}_2\text{O} = \text{CO}_2$. H_2 in moist H_2 :CO (1:1) mixtures. Addition of traces of K_2CO_3 to catalysts promoted with Al_2O_3 preferentially accelerated the latter reaction. L. J. J.

Oxidation processes. XVII. Autoxidation of ascorbic acid in the presence of copper. A. Weissberger and J. E. Lu Valle (*J. Amer. Chem. Soc.*, 1944, 66, 700–705).—The autoxidation rates of l-ascorbic acid (I) in presence of Cu throughout the pH range 2.59 to 9.31 is in accord with the assumption that 1 mol. of dehydro-ascorbic acid and one of H_2O_2 are formed from one of (I) and one of O_2 . The rate (2×10^{-6} g.-mol. per l.) is not \propto (I) concn., but \propto $[\text{O}_2]$; it \propto increase in $[\text{Cu}]$ at higher concns. of Cu, but at lower concns. it increases faster than $[\text{Cu}]$. The dependence of the rate on pH is caused by complex formation of some of the buffers with the Cu. Only the univalent ion of (I) acts as substrate of the Cu catalysis. A non-chain mechanism for the catalytic reaction is discussed. W. R. A.

Oscillographic polarography. J. Heyrovsky and J. Forejt (*Z. physikal. Chem.*, 1943, A, 193, 77–96).—Electrolytic polarisation phenomena can be very clearly demonstrated by means of a polarisable Hg electrode with an alternating e.m.f. and electron-beam oscillograph. Dropping and streaming Hg electrodes were used, the latter consisting of a jet of Hg forced under 1–2 atm. through a 0.1-mm. orifice obliquely through the solution examined. The action of depolarisers at concn. $<10^{-4}\text{N}$. can be studied by means of the first derivative of the potential-time curve, obtained oscillographically. Most metals are deposited at approx. the same rate,

and the more slowly the higher is the a.c. frequency. No deposition is observed at frequencies >1600 Hertz. The anodic reaction of Hg^{++} with Cl^- and CN^- vanishes at 400 Hertz. Zn is deposited most rapidly from NH_3 solutions, less rapidly from acid and least from alkaline solutions. Cd is relatively slowly deposited from KCN solutions. Corresponding results are obtained by the use of amalgamated Hg dropping electrodes. L. J. J.

Mechanism of emission of ultra-violet radiation by anodic polarisation. R. Audubert (*Compt. rend.*, 1943, 216, 880—882; cf. A., 1933, 764).—Ultra-violet light is emitted when an anode of Al, Ta, Mg, or Si is polarised. It is possible that this is due to reactions between activated and non-activated OH^* . It is possible to calculate the ν of emission if the level of activation of the OH^* is known. Reducing agents in the anode liquid suppress or weaken the luminosity. Possible reactions considered are: $\text{OH} + \text{OH}^* \rightarrow \text{H}_2\text{O} + h\nu_1$; $\text{OH} + \text{OH}^* \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + h\nu_2$; $\text{OH}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}_2 + h\nu_3$; $\text{OH}^* + \text{OH}^* \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + h\nu_4$. The vals. of λ corresponding to the energy evolved in these reactions are 2187, 1895, 1458, and 1304 Å., respectively. In the actual spectrum, investigated by means of a CuI counter, bands occur at 1950, 2190, 2390, and 2530 Å., independent of the anodic potential, the nature of the electrode and the electrolyte. Two of these bands correspond with theory. It is possible that the third and fourth of the above reactions give out part of their energy thermally, the photon liberated being due to the deactivation of two OH^* . This would give a band at 2370 Å., which is in the neighbourhood of another of the observed bands. A. J. M.

Interpretation of photolysis of alkali azides in aqueous solution. M. Bonnemay (*Compt. rend.*, 1943, 216, 882—884).—Possible reactions in the photolysis of azides in aq. solution are: $\text{N}_3^+ + h\nu = (\text{N}_3^+)^0$; $\text{H}_2\text{O} + (\text{N}_3^+)^0 + h\nu = \text{N}_2^* + \text{NH} + \text{OH}^*$; $\text{H}_2\text{O} + \text{N}_2^* + \text{N}_3^+ = \text{N}_2^* + \text{N}_2 + \text{NH} + \text{OH}^*$; $\text{H}_2\text{O} + \text{N}_2^* + (\text{N}_3^+)^0 = \text{N}_2^* + \text{N}_2 + \text{NH} + \text{OH}^*$; $(\text{N}_3^+)^0 = \text{N}_3^+$; $\text{N}_2^* = \text{N}_2 + h\nu_1$. $(\text{N}_3^+)^0$ represents a form of N_3^+ which is directly decomposable and of which the life is ~ 5 min. The radicals (NH) react between themselves and with H_2O to give secondary products. Equations for the kinetics of these reactions are obtained which give results agreeing with experiment. A. J. M.

Photosensitised reactions of ethylene. D. J. Le Roy (*Canad. Chem.*, 1944, 28, 430—431, 451).—A review. The technique of photosensitisation is described, and the variation in results obtained by using Xe, Cd, Hg, Zn, and Na as photosensitisers is outlined. The Hg-photosensitised polymerisation of C_2H_4 (A., 1942, I, 151) is discussed. The Cd-photosensitised reaction produces little C_2H_2 and H_2 (Steacie *et al.*, *ibid.*, 372). With Zn ($^1\text{P}_1$) atoms the primary process is almost entirely $\text{Zn}(^1\text{P}_1) + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_3 + \text{H} + \text{Zn}(^1\text{S}_0)$ (Habeeb *et al.*, *ibid.*, 304). A. J. M.

Application of probability considerations to the mechanism of the photochemical polymerisation of acetylene. B. L. Dunicz (*J. Chem. Physics*, 1944, 12, 204).—Erratum (cf. A., 1944, I, 132). L. J. J.

Photochemical studies. XXXVII. Tests of mechanism for the photochemical decomposition of acetone. J. J. Howland, jun., and W. A. Noyes, jun. (*J. Amer. Chem. Soc.*, 1944, 66, 974—977).—The photochemical decomp. of COMe_2 has been investigated at 27° using $\lambda\lambda$ 2500—2700 and 3130 Å., and various pressures. The quantum yield of COMe_2 decomposed diminishes with increasing intensity at all $\lambda\lambda$. Decrease in the size of the reaction vessel leads to an increase in $\text{C}_2\text{H}_2/\text{CO}$ ratio; this ratio is diminished with increasing pressure at high intensity. These data are discussed in the light of the conflicting mechanisms proposed by Herr and Noyes (A., 1940, I, 417) and Spence and Wild (A., 1941, I, 480) and favour the former. W. R. A.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Non-stoichiometric equations. O. F. Steinbach (*J. Chem. Educ.*, 1944, 21, 66, 69).—Examples of chemical equations that can be made to balance algebraically by using different sets of coeffs. with only one set representing the stoichiometric equation are given. The correct stoichiometric coeffs. are obtained when the equations are balanced by either the valency-change or the ion-electron methods. L. S. T.

Existence of lithium hydrogen carbonate. (Mlle.) L. Lagarde (*Compt. rend.*, 1943, 216, 810—812).—The solubility of Li_2CO_3 in H_2CO_3 has been studied for various pressures of CO_2 (5—800 mm.). Combining the law of mass action with Henry's law reasonably good vals. of the const. are obtained, indicating the existence of LiHCO_3 in solution. A. J. M.

Transformations of vitreous sodium metaphosphate. A. Boule (*Compt. rend.*, 1943, 216, 890—892).—Na and K metaphosphates behave very differently when heated. In the case of Na, the insol. forms (referred to as B and D) and Graham's salt (metallic vitreous) always afford a sol. trimetaphosphate. When this is fused at 640° it gives a liquid metaphosphate formerly described (A., 1935, 571, 591, 944). In the case of K salts, the sol. forms (trimeta- and

tetrameta-) and the pptd. amorphous form are always converted into an insol. salt when heated. A. J. M.

Isotope enrichment by diffusion of copper into silver sulphide. A. Klemm (*Z. physikal. Chem.*, 1943, A, 193, 29—39).—Isotope separation coeffs. are calc. for the general case of diffusion of an element across a plane boundary. A 5.5% change in the isotopic distribution ratio of Cu has been found after diffusion into Ag_2S at 450°. L. J. J.

Complex compounds of biguanide with tervalent metals. XI. Silver (Ag^{III}) ethylenedibiguanide hydroxide and its salts. P. Ray and K. Chakravarty (*J. Indian Chem. Soc.*, 1944, 21, 47—50).—The composition of a complex silver ethylenedibiguanide hydroxide and its salts, in which the quadricovalent Ag shows a primary valency of 3, is $[\text{Ag}^{\text{III}} \text{En}(\text{BigH}^+)_2]\text{X}_3$, where $\text{X} = \frac{1}{2}\text{SO}_4$, NO_3 , ClO_4 , or OH and $\text{En}(\text{BigH})_2 = 1$ mol. of ethylenedibiguanide, $\text{C}_6\text{H}_{12}\text{N}_{10}$. The salts are quite stable at ordinary temp. and the nitrate can be cryst. from warm dil. HNO_3 . The compounds liberate 2 equivs. of I for every atom of Ag from acidified KI solution. The new complex is diamagnetic. Ag^{III} thus resembles Au^{III} in forming quadricovalent planar complexes of the penetration class. F. R. S.

Calcium oxalates. (Dehydration curves, X-ray and infra-red studies.) J. Lecomte, (Mlle.) T. Pobeguine, and J. Wyart (*Compt. rend.*, 1943, 216, 808—810).—The dehydration of four hydrates of CaC_2O_4 has been investigated. The hydrates were the monohydrate (I), and the three trihydrates, (II) (obtained by evaporation of solution in HCl), (III) (from aq. solution), and (IV) (the trihydrate of Jakob *et al.*). At ordinary temp. (I) and (II) do not lose H_2O over P_2O_5 ; (III) rapidly loses 4—5% in wt., but regains this on exposure to air; (IV) gradually loses wt. up to 18%. Loss of H_2O at higher temp. has also been studied. The distances between lattice planes in the anhyd. salt and the four hydrates, and a qual. estimate of the intensity of the spots in the Debye-Scherrer diagram, are given. The position and intensity of the infra-red bands are also given. The methods show clearly that the five substances considered are quite distinct. Part of the H_2O of (III) is less strongly held than the rest. Loss or gain of this H_2O does not affect the lattice. A. J. M.

Crystallographic structure of precipitated mixtures of calcium and strontium carbonates. Their fractional decomposition by heat. M. Guichard and J. Wyart (*Compt. rend.*, 1943, 216, 844—846).—The X-ray structures of CaCO_3 and SrCO_3 are different when the substances are pptd. pure, and when they are pptd. together from mixed solutions of CaCl_2 and SrCl_2 . In the latter case the diagram obtained depends also on the composition of the mixed solutions. It is possible to obtain a compound $\text{CaSr}(\text{CO}_3)_2$, which X-ray analysis shows to be orthorhombic. If a mixture of CaCO_3 and SrCO_3 prepared from the single substances is heated to 855°, the curve of loss of wt. with time is made up of two distinct parts. SrCO_3 begins to decompose at this temp. slowly, and only after all the CaCO_3 has been decomposed. When the ppt. obtained from the mixed solutions is heated, the curve of loss of wt. against time shows no discontinuity. There is, however, a decrease in velocity when $\sim 85\%$ of the CaCO_3 has been decomposed, but the substance decomposes as a whole. X-Ray diagrams of the substance obtained from a mixed solution which would give $3\text{CaCO}_3, 2\text{SrCO}_3$ show the product to be a mixture of rhombohedral CaCO_3 and orthorhombic $\text{SrCa}(\text{CO}_3)_2$. A. J. M.

Crystalline magnesium and ferrous hydroxides. L. M. Clark, A. G. M. Hedley, and J. G. Robinson (*J. S.C.I.*, 1944, 63, 208—210).—Cryst. $\text{Mg}(\text{OH})_2$ can be prepared continuously by slowly mixing sufficiently dil. solutions of Mg^{++} and OH^- in presence of brucite seed. $\text{Fe}(\text{OH})_2$ can be similarly made, in the absence of O_2 , from Fe^{++} and OH^- , using initially seed crystals of the isomorphous $\text{Mg}(\text{OH})_2$. These cryst. products settle and filter well. The X-ray pattern of cryst. $\text{Fe}(\text{OH})_2$ has been obtained, and from it the unit cell dimensions are deduced as a 3.24, c 4.47 Å.

Basic magnesium nitrates. (Mme.) L. Walter-Lévy (*Compt. rend.*, 1943, 216, 846—847).—The composition of the ppt. obtained by adding an alkali carbonate or hydroxide to fairly conc. solutions (4—5M.) of $\text{Mg}(\text{NO}_3)_2$ is const. no matter what precipitant is used, or what quantity, and corresponds to $\text{Mg}(\text{NO}_3)_2, 4\text{Mg}(\text{OH})_2$. The X-ray diagram of this compound is different from that of the nitrate-carbonate, $\text{Mg}(\text{NO}_3)_2, 2\text{MgCO}_3, 8\text{H}_2\text{O}$, and from that of brucite. When more dil. solutions are used, the stable solid phase is $\text{Mg}(\text{OH})_2$. A. J. M.

Crystallised basic zinc chromates. O. F. Tarr, M. Darrin, and L. G. Tubbs (*J. Amer. Chem. Soc.*, 1944, 66, 929—930).—Basic Na, K, and NH_4 Zn chromates were prepared by the reaction between an aq. suspension of ZnO and a solution of the appropriate tetrachromate ($\text{K}_2\text{Cr}_2\text{O}_7$). They were well-defined crystals having the composition $\text{M}_2\text{O}, 4\text{ZnO}, 4\text{CrO}_3, 3\text{H}_2\text{O}$. Corresponding alkaline-earth compounds were not obtained by this method. W. R. A.

“Sainte-Claire Deville hot-cold tube” and some of its applications. R. C. Young (*J. Chem. Educ.*, 1943, 20, 378, 380).—The use of the hot-cold tube for the prep. of TiCl_4 , ZrBr_4 , Si_2Cl_7 , TaBr_5 , and TiBr_3 is described. L. S. T.

pH corresponding to the threshold of precipitation of rare-earth elements. (Mme.) M. Trombe (*Compt. rend.*, 1943, 216, 888—890).—The pH at which pptn. of rare-earth elements first occurs has been determined by slowly dissolving NH_3 in a solution of the nitrate of the element concerned. At first a colloid is obtained. At the moment of coagulation the pH falls suddenly, and then increases very slowly as the concn. of metal ions decreases. The pH for the threshold of pptn. of the Ce elements are > those obtained by Britton (A., 1925, ii, 1203) for the same concn. The change of threshold pH with concn. (ΔpH) varies for the different elements. In the range of concn. considered (0.5—0.005M.) ΔpH is La 1.44, Pr 0.85, Nd 0.65, Sa 0.39, Gd 0.80, Dy 0.75, Yb 1.25, Y 2.14.

A. J. M.

Chloro(iso)cyanates of silicon, including rearrangements at high temperatures. H. H. Anderson (*J. Amer. Chem. Soc.*, 1944, 66, 934—935).—The chloro(iso)cyanates $\text{SiCl}_3(\text{NCO})$, $\text{SiCl}_2(\text{NCO})_2$, and $\text{SiCl}(\text{NCO})_3$, b.p. 86–8°, 117–8°, 152–0°, have been prepared as colourless liquids by (a) interaction of SiCl_4 and $\text{Si}(\text{NCO})_4$ at 600°, (b) interaction of SiCl_4 and $\text{Si}(\text{NCO})_4$ in a sealed tube at 135° for 70 hr., (c) gradual addition of AgNCO to a large excess of SiCl_4 in CS_2 – EtBr (1:2). Vals of m.p., ρ_{25}^{20} , and mol. vol. are given and compared with those of SiCl_4 and $\text{Si}(\text{NCO})_4$. $\text{SiCl}(\text{NCO})_3$ cannot be prepared by (c). Rearrangements at 600° without a catalyst display random distribution.

W. R. A.

Enrichment of ^{15}N by chemical exchange. K. Clusius and E. Becker (*Z. physikal. Chem.*, 1943, A, 193, 64—76).—Enrichment of ^{15}N to 6.0% has been attained by means of the equilibrium $^{15}\text{NH}_3(\text{liq.}) + ^{14}\text{NH}_3(\text{gas}) \rightleftharpoons ^{14}\text{NH}_3(\text{liq.}) + ^{15}\text{NH}_3(\text{gas})$ in two stages. 60% NH_4NO_3 solution is saturated with NH_3 at 90 mm. pressure in two packed towers in series, with gas and liquid flowing in the same direction. The NH_4NO_3 is continuously decomposed with NaOH and the NH_3 recirculated.

L. J. J.

Reactions of hyponitrites. I. Action of charcoal on sodium nitrite etc. T. M. Oza (*J. Indian Chem. Soc.*, 1944, 21, 71—78).—When charcoal is heated with NaNO_2 , $\text{Na}_2\text{N}_2\text{O}_2$ is produced to an appreciable extent as an intermediate product, although the quantity decreases at higher temp. The reaction consists of two concurrent reactions, the first being the thermal decomp. of NaNO_2 , accelerated by C: $4\text{NaNO}_2 + 3\text{C} = 2\text{Na}_2\text{CO}_3 + \text{CO}_2 + 2\text{N}_2$. The second is the reduction of NaNO_2 to $\text{Na}_2\text{N}_2\text{O}_2$, and production of N_2O from the latter: $2\text{NaNO}_2 + \text{C} = \text{Na}_2\text{N}_2\text{O}_2 + \text{CO}_2$, $\text{Na}_2\text{N}_2\text{O}_2 + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{N}_2\text{O}$. The last reaction occurs even at room temp. $\text{Na}_2\text{N}_2\text{O}_2$ will remove traces of CO_2 from air, and this is one reason why it is difficult to keep. The thermal decomp. of $\text{Na}_2\text{N}_2\text{O}_2$ has also been investigated. The decomp. proceeds readily at 334—336°. The primary reaction appears to be $3\text{Na}_2\text{N}_2\text{O}_2 = 2\text{Na}_2\text{O} + 2\text{N}_2 + 2\text{NaNO}_2$, but this is followed by the autoxidation of the NaNO_2 : $5\text{NaNO}_2 = \text{Na}_2\text{O} + 3\text{NaNO}_3 + \text{N}_2$.

A. J. M.

Complex between sulphuric and nitric anhydrides which dissociates liberating nitric acid. M. Dode (*Compt. rend.*, 1943, 217, 153—155).—When SO_3 is added to 100% HNO_3 at -10° , a cryst. compound, $5\text{SO}_3 \cdot 2\text{N}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, is formed, which when warmed dissociates into HNO_3 and not N_2O_5 , although SO_3 is present. The reaction is $4(5\text{SO}_3 \cdot 2\text{N}_2\text{O}_5 \cdot 2\text{H}_2\text{O}) \rightarrow 6\text{HNO}_3 + 5(4\text{SO}_3 \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O})$. It is reversible.

A. J. M.

Effect of pH on the composition and physical appearance of potassium molybdates. H. Guiter (*Compt. rend.*, 1943, 216, 796—798; cf. *ibid.*, 1943, 216, 587).—The variation of p in the formula $\text{MoO}_3 \cdot p\text{K}_2\text{O}$ with pH of the solution has been investigated. In presence of HCl , $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ppts. from $n\text{-K}_2\text{MoO}_4$ at pH < 2.6. At pH -0.7 to 0.7 KCl appeared after 1—3 months. For negative vals. of pH a very viscous gum was formed after ~4 months. When dried this gave MoO_3 . At pH 0.7—7, the compound $7\text{MoO}_3 \cdot 3\text{K}_2\text{O} \cdot 22\text{H}_2\text{O}$ (I) was obtained after 3 weeks, and KCl crystallised after 2 months. In presence of AcOH , (I) appeared in solutions of pH 2.8—7 after 3 weeks, and at pH 6.3—11.6 a white cryst. compound, $4\text{MoO}_3 \cdot 3\text{K}_2\text{O} \cdot 2\text{H}_2\text{O}$, was formed after 2 months. In solutions of pH > 7 the normal anhyd. K_2MoO_4 was formed. The largest crystals were obtained in a solution of pH 13.5. This behaviour is different from that of Na molybdates, with which the K salts are not isomorphous.

A. J. M.

Double molybdates and tungstates of alkali metals with lanthanum or bismuth. L. G. Sillen and H. Sundvall (*Arkiv Kemi, Min., Geol.*, 1943, 17, A, No. 10, 18 pp.).—Two types of double salts with the general formula $\text{AM}(\text{XO}_4)_2$ (isomorphous with scheelite) and $\text{A}_2\text{M}(\text{XO}_4)_4$ (closely related to scheelite) have been prepared. The compounds with their lattice consts. (a and c respectively) are $\text{LiLa}(\text{MoO}_4)_2$ 5.307, 11.670; $\text{NaLa}(\text{MoO}_4)_2$ 5.328, 11.699; $\text{KLa}(\text{MoO}_4)_2$ 5.420, 12.114; $\text{LiLa}(\text{WO}_4)_2$ 5.335, 11.629; $\text{NaLa}(\text{WO}_4)_2$ 5.345, 11.632; $\text{KLa}(\text{WO}_4)_2$ 5.443, 12.034; $\text{LiBi}(\text{MoO}_4)_2$ 5.232, 11.495; $\text{NaBi}(\text{MoO}_4)_2$ 5.267, 11.552; $\text{KBi}(\text{MoO}_4)_2$ 5.380, 11.916; $\text{Na}_3\text{La}(\text{WO}_4)_4$ 11.600, 11.546; $\text{Na}_3\text{Bi}(\text{MoO}_4)_4$ 11.444, 11.520; $\text{Na}_3\text{Bi}(\text{WO}_4)_4$ 11.520, 11.402 Å.

C. R. H.

Extraction of uranium from Canadian pitchblende. A. Knebel (*J. Chem. Educ.*, 1944, 21, 148—149).—The laboratory procedure

described involves removal of U as crude sulphate from pitchblende concentrate and the purification of the crude sulphate. L. S. T.

Formation of iodosic acid by the action of iodine on silver nitrate. (Mlle.) M. L. Josien (*Compt. rend.*, 1943, 216, 842—844; cf. A., 1936, 438).—Aq. AgNO_3 is added to a solution of I in KI in sufficient quantity to remove all free I. When equilibrium has been established, the liquid is filtered and three separate portions are respectively titrated with As_2O_3 and with $\text{Na}_2\text{S}_2\text{O}_3$, and completely converted into HIO_3 and the oxidising power determined. Results indicate that HIO_2 exists together with HIO_3 and HOI in the product of the action of I on AgNO_3 .

A. J. M.

Action of hydrogen sulphide on permanganates. H. Potassium, ammonium, and barium permanganates. S. Mohammad and S. N. Bedi (*J. Indian Chem. Soc.*, 1944, 21, 55—60; cf. A., 1942, I, 70).—When aq. H_2S is added to 1% aq. KMnO_4 until the colour just disappears, a neutral solution and a dark brown ppt. are obtained. The former contains 65% of the K as $\text{K}_2\text{S}_2\text{O}_8$, $\text{K}_2\text{S}_2\text{O}_4$, and K_2SO_4 . Further addition of H_2S after the decolorisation stage makes the solution alkaline owing to hydrolysis of permanganite. Excess of H_2S produces K polysulphides, and converts the dark brown ppt. into MnS . Similar results are obtained for the solutions produced with NH_4MnO_4 and $\text{Ba}(\text{MnO}_4)_2$. In the ppt. the ratio $\text{K}_2\text{O}/\text{MnO}_2 = 1/2$, but the ratios $\text{K}_2\text{O}/\text{MnO}$ and MnO/MnO_2 are variable. The action of H_2S on $\text{K}_2\text{O} \cdot 8\text{MnO}_2$, prepared as a dark brown ppt. by adding 2.5 c.c. of a 10% solution of glycerol to 50 c.c. of 1% KMnO_4 , was also studied. The same products were obtained as with KMnO_4 , but K_2SO_4 was absent from the solution before the polysulphide stage was reached. Similar results were obtained by adding H_2S to $\text{BaO} \cdot 2\text{MnO}_2$, prepared by adding H_2O_2 to a 1% solution of $\text{Ba}(\text{MnO}_4)_2$ until just decolorised. In the action of H_2S on NH_4MnO_4 , the ratio of $(\text{NH}_4)_2\text{O}/\text{MnO}_2$ in the ppt. is 1/1 instead of 1/2 with the other permanganates.

A. J. M.

Influence of the atmospheric factors of production on the chemical activity and the grain distribution of powders. J. A. Hedvall and A. Lundberg (*Arkiv Kemi, Min., Geol.*, 1943, 17, A, No. 12, 11 pp.).—Previously published work on the effect of the gas pressure used in the prep. of powders on the chemical properties of the powders is reviewed, and new data on the properties of Fe_2O_3 and CaO prepared in vac. and under normal air pressure are presented. The vac.-prepared oxides give a smaller proportion of particles of grain size 0—~15 μ , and a larger proportion of particles of size > ~15 μ , than do oxides prepared under ordinary pressure. The powders with the larger proportion of small particles are more reactive towards solvents than those with a smaller proportion. This difference in reactivity is not wholly accounted for by differences in surface area.

C. R. H.

Reductions with nickel-aluminium alloy and aqueous alkali.—See A., 1944, II, 258.

XI.—GEOCHEMISTRY.

Determination of the helium content of terrestrial materials. C. Goodman and R. D. Evans (*Rev. Sci. Instr.*, 1944, 15, 123—128).—Results obtained with 133 rocks of representative types are summarised; the He content ranges from 0.25×10^{-5} to 65×10^{-5} with modal and median vals. of 1.8×10^{-5} c.c. of He per g. There appears to be no correlation between He content and rock or mineral type, except for minerals in which U and Th are > 0.1% (cf. C., 1944, Part 4).

L. S. T.

Standard thermal dehydration curves of minerals. P. G. Nutting (*U.S. Geol. Surv. Prof. Paper* 197-E; *Builld. Sci. Abs.*, 1944, 17, No. 226).—From several hundred curves obtained over a period of 15 years, 73 typical curves are chosen and reproduced in 9 main groups. Each mineral is described and similarities and differences within the groups of curves are noted.

J. A. S.

Occurrence of chloritoid in the Tumkur district, Mysore State. C. S. Pichamuthu (*Current Sci.*, 1943, 12, 332).—The Chitaldrug Dharwar schist belt in the Tumkur district contains chloritoid (I), which occurs in disc-like, lenticular shape. It has almost perfect basal cleavage; imperfect prismatic cleavages intersect at angles of 120° and there is a parting parallel to 010 . Crystalloblasts of (I) occur in the rock without relation to the direction of schistosity. (I) is poeciloblastic and contains much quartz and ilmenite. It is pleochroic and has a high relief but low birefringence. $\gamma - \alpha = 0.009 - 0.01$. The direction Z makes an angle of 9° with the normal to 001 . The optic sign is positive and twinned crystals are common.

J. O'M-B.

Unusual features in ejected blocks at Kilauea volcano. G. A. Macdonald (*Amer. J. Sci.*, 1944, 242, 322—326).—Picroitic basalts near the feeding conduit of this volcano appear to have been reconstituted in solid state as a result of remaining at a high temp. for a long period, during which the original pigeonite broke down to give hypersthene and augite. A reddened picroitic basalt shows deposition of Fe ore throughout the olivine phenocrysts.

L. S. T.

A I—General, Physical, and Inorganic Chemistry.

NOVEMBER, 1944.

I.—SUB-ATOMICS.

Stark effect in hyperfine structure of sodium D lines. H. Angenetter (*Naturwiss.*, 1943, 31, 112—113).—The quadratic Stark effect is calc. quantum-mechanically from the hyperfine structure. L. J. J.

Stark effect of the hyperfine structure of sodium. F. Gabler (*Naturwiss.*, 1943, 31, 42—43).—The method formerly used (A., 1942, 1, 254) for studying the inverse Stark effect, using an at. beam as absorbing medium, has been improved and used for the investigation of the Stark effect of the hyperfine structure of Na. The Stark effect of the D lines is a quadratic effect. The π and σ components of the D_1 line are displaced equally towards longer λ by a field of 100 kv. per cm. In the case of D_2 , each hyperfine component splits into a π and two σ components. The weak σ_2 line and the π line are displaced by approx. the same amount to the red, but the strong σ_1 line is displaced by only about one third of this distance. A. J. M.

K-Absorption spectra of elements of atomic numbers 72 (Hf), 73 (Ta), 74 (W), 75 (Re), 76 (Os), and 77 (Ir). (Mlle.) I. Manescu (*Compt. rend.*, 1943, 216, 732—734).—Vals. of λ and ν/R for K -absorption edges are given for these elements. A. J. M.

Penetration of foils by electrons of high energy. K. T. Chao (*Sci. Rec. [Acad. Sinica]*, 1942, 1, 129—131).—Electrons with various incident energies up to 7 Me.v. penetrate foils of C (thickness = $t = 0.5$ cm.), Al ($t = 0.0355$ cm.), mica ($t = 0.05$ cm.), Pt ($t = 0.0004$ cm.), Pb ($t = 0.0038$, 0.006, and 0.05 cm.), and the transmitted intensities for the electron energies are measured experimentally and calc. theoretically. Results are compared. The experimental data for Pb, Pt, and mica [$H_2KAl_3(SiO_4)_3$] are in good agreement with the theory, but with C and Al the experimental vals. are < the theoretical. L. S. G.

Change of position of thorium in the periodic system. G. E. Villar (*Anal. Assoc. Quim. Argentina*, 1943, 31, 213—221).—Arguments are advanced for the existence of a series of "rare-earth" elements in the position occupied by Ac. The chemical and physical properties of Th agree with this. The at. mass of an element is shown to be < the average of the at. mass of its neighbours in the same group of the periodic system, and this relation is universally true only if Th, Pa, and U all occupy the same position as Ac. F. R. G.

Analysis of β -disintegration data. I. The Sargent curves and Fermi and Konopinski-Uhlenbeck theories of beta-radioactivity. C. S. Wang and W. Y. Chang. II. Probability of β -disintegration and the complexity of atomic nuclei. W. Y. Chang and C. S. Wang (*Sci. Rec. [Acad. Sinica]*, 1942, 1, 98—103, 103—108).—I. The Sargent curves are plotted for a no. of β -emitters. The radioactive elements group themselves more closely into Sargent curves when the positive and negative emitters are plotted separately. A comparison is made with the Fermi theory and the Konopinski-Uhlenbeck theory of β -decay, calculations being made of $|M|^2/\tau_0$ for each element, where M is the matrix element of the heavy particle and τ_0 is the universal decay time. The vals. of $|M|^2/\tau_0$ fall into groups of different orders of magnitude, viz., 10^{-24} , 10^{-26} , and 10^{-28} or 10^{-25} , 10^{-27} , and 10^{-29} according as to whether Fermi's or Konopinski and Uhlenbeck's form of interaction is taken. The classification of $|M|^2/\tau_0$ is satisfactory and there is good agreement between theory and experiment.

II. The vals. of τ_0 and $|M|^2$ for ^4He are calc. the latter being compared with that of Gronblom. The difference in $|M|^2$ between positive and negative emitters is discussed and interpreted. The variation of $|M|^2$ with at. no., Z , is due to the greater rearrangement of the nuclear constituents after a β -transition as Z increases. The effect of isotope number and of a nuclear Coulomb field in the theory of β -disintegration is studied, and it is verified that the decay const. of positive emitters decreases while that of negative emitters increases with the isotope no. The selection rules for different β -transformations are also studied. L. S. G.

Sargent curves for artificially β -active nuclei. P. K. S. Chaudhury (*Indian J. Physics*, 1943, 17, 262—270).—Sargent curves of β -active nuclei have been drawn and used to deduce the approx. spin of nuclei of even mass no. The utility of these curves in studying nuclear isomerism is pointed out. W. R. A.

Lost radioactivity of caesium. W. Wahl (*Naturwiss.*, 1943, 31, 18—19; cf. Hahn *et al.*, A., 1943, I, 46).—The occurrence of a line corresponding to a mass no. of 132 in the mass-spectrogram of pollicite is confirmed, and the possible mols. or radicals which could give rise to this line are discussed. It appears to be due to ^{132}Ba , although this was not found by Hahn *et al.* A. J. M.

Lost radioactivity of caesium. O. Hahn, F. Strassmann, J. Mat-
tauch, and H. Ewald (*Naturwiss.*, 1943, 31, 19).—A reply to Wahl (see preceding abstract). A. J. M.

Natural and artificial activity of lutecium, a new case of isomerism. A. Flammersfeld and J. Mat-
tauch (*Naturwiss.*, 1943, 31, 66—67).—Irradiation of Lu with neutrons gives activities of half-life 3.4 ± 0.1 hr. and 6.6 ± 0.05 days. β -Ray absorption measurements give energy 1150 ke.v. and 4.40 ke.v., respectively. The long-life initial activity is 3 times that of the short-life with slow neutrons. The former is obtained only with thermal, the latter with both thermal and resonance, neutrons. Hence the two substances are not isomeric. Naturally active Lu gives β -rays of energy 400 ke.v., together with a harder radiation (γ -radiation). It is concluded that the 6.6-day substance is isomeric with ^{176}Lu , and the 3.4-hr. substance has mass no. 177. L. J. J.

New gaseous product of uranium fission. W. Seelmann-Eggebert and H. J. Born (*Naturwiss.*, 1943, 31, 59—62).—Two new Kr isotopes of half-life 75 min. and 4.6 hr., obtained respectively from 50-sec. Br and 3-min. Br, are described. 30-sec. I gives a 3.8-min. Xe. The max. energy of the 75-min. Kr is ~ 4 Me.v., that of the 4.6-hr. Kr is ~ 0.8 Me.v., and that of the 3.8-min. Xe is 4 Me.v. L. J. J.

Identification of uranium fission products with corresponding isotopes obtained by means of (na) and (np) processes. H. J. Born and W. Seelmann-Eggebert (*Naturwiss.*, 1943, 31, 86—89).—Irradiation of Rb and Sr salts with fast Li-D neutrons gives Kr isotopes by (na) and (np) processes. Sr gives one isotope with half-life 4.6 hr., Rb gives two with half-lives 4.6 hr. and 75 min. The identity of the Kr isotopes with those of the same half-lives from U is established by comparison of the absorption of emitted β -rays. The respective mass nos. 85 and 87 are ascribed to the two isotopes. The 30-min. Br from U is identical with a Br obtained from Rb by a (na) process. L. J. J.

Life of the mesotron. G. Cocconi and V. Tongiorgi (*Naturwiss.*, 1943, 31, 108—109).—Measurement of mesotron fine structure at 2200 m. above sea level at Passo Sella in the summer of 1942, at angles 0° , 25° , 40° , 50° , and 60° to the zenith, showed no variation in $\tau/\mu c$, where τ and μ are the life and rest mass of the mesotron. The val. 3.4×10^{-8} sec. per Me.v. was found for $\tau/\mu c$. L. J. J.

Life of the mesotron. J. Juilfs (*Naturwiss.*, 1943, 31, 109—110).—A reply to Cocconi (see above). The measurements quoted do not exclude the presence of mesotrons of short life. L. J. J.

Presence of mesotron showers in extended showers in air. G. Cocconi, A. Loverdo, and V. Tongiorgi (*Naturwiss.*, 1943, 31, 135—136).—In order to confirm the existence of extended showers of considerable penetrating power, and to investigate the connexion between them and the Auger electron showers, an apparatus using 8 groups of counters was employed. Almost all the penetrating showers are composed of electrons and mesons, and contain at least two mesons. A. J. M.

The meson-pair theory of nuclear interaction. O. Klein (*Archiv Mat. Ast. Fys.*, 1944, 30, A, 3, 13 pp.).—A modification is made of Marshak's "heavy electron" pair theory of nuclear forces in which the "heavy electrons" (obeying the ordinary relativistic Dirac equation) are replaced by mesons of integer spin and Bose statistics. The results are similar to those of Marshak, whose assumptions, however, do not contradict the known spin and statistical properties regarding the disintegration of mesons in cosmic rays. As in Marshak's theory, there is no indication of the origin of the β -electrons, which is naturally explained by Kemmer's "symmetrical" theory, nor of the non-Dirac magnetic moments of protons and neutrons, especially their opposite sign and approx. equality. To solve these difficulties it would probably be necessary to assume additional interactions in the pair theory.

Second maximum of the Rossi curve. M. Forró and Z. Ozorai (*Naturwiss.*, 1943, 31, 140).—An improved apparatus similar in design to that originally used by Schmeiser *et al.* (cf. A., 1938, I, 291) was used to detect the existence of the second max. of the Rossi curve. Between 5 and 24 cm. Pb no max. could be observed within the limit of error of 1–2%.

A. J. M.

The impulse-energy tensor of material particles. I. Mesons and electrons. II. Particles of spin 2 or 3/2. T. S. Chang (*Proc. Roy. Soc.*, 1944, A, 182, 302–311, 311–318).—I. The investigation gives a direct and general construction of a real, symmetrical tensor T_{ik} the divergence of which to i is -1 times the four-force f_k experienced by the matter. Interpreting T_{ik} as the impulse-energy tensor for the case of no electro-magnetic field the energy-momentum density obtained from T_{ik} is compared with that obtained by treating $(\hbar/i)(\delta/\delta x_k)$ as the energy-momentum operator. In the general case the Hamiltonian of the matter is compared with $\int T_{44} dV dy dz$. The compared quantities agree apart from unimportant modifications.

II. Calculations of a general impulse-energy tensor T_{ik} are extended to particles of spin 2 or 3/2, the wave equations of which were given by Fierz and Pauli. Results are generally similar, but the expression for is very complicated.

G. D. P.

II.—MOLECULAR STRUCTURE.

Band spectrum of nitrogen: new singlet systems. A. G. Gaydon (*Proc. Roy. Soc.*, 1944, A, 182, 286–301).—Five new systems due to N_2 are observed in a mildly condensed discharge through nitrogen. Rotational analyses of some of the bands are made and it is shown that all correspond to transitions to the upper level $a^1\Pi_u$ of the Lyman-Birge-Hopfield system. An additional progression of the system studied by Van der Ziel (the fifth positive system) is found, necessitating revision of the upper vibrational quantum nos. Some of Kaplan's systems are also examined and the rotational analysis of one shows that it corresponds to a transition to the lower level of the fifth positive system. This level probably lies a little below $a^1\Pi_u$ and is metastable; it may play a part in the formation of active N . Rotational and vibrational consts. for the singlet electronic states of N_2 are tabulated.

G. D. P.

Development of δ - and γ -bands of nitric oxide in active nitrogen and Lyman bands in helium-nitrogen mixture. B. M. Anand (*Indian J. Physics*, 1943, 17, 246–251).—The doublet structure of 0-0, 0-1, 0-2, and 0-3 bands of the δ system ($^2\Sigma \rightarrow ^2\Pi$) of NO and of 1-0 and 2-0 bands of the γ system ($A^2\Sigma \rightarrow ^2\Pi$), as observed in active N, has been measured and is described. β bands of NO are not found in the afterglow of active N. Three new bands, 6-13, 0-8, and 4-9, of the Lyman-Birge-Hopfield system of N_2 are developed in a mixture of He and N_2 .

W. R. A.

Pressure widening of the rotation-vibration bands of the HCN molecule at 10,385 Å. G. Kortüm and H. Verleger (*Naturwiss.*, 1943, 31, 44).—The broadening of the fine structure of the rotation-vibration bands of HCN with increasing pressure, and the effect of addition of foreign gases, have been investigated, in order to discover the effect of intermol. forces on the sharpness of energy levels. In the range 75–550 mm. the pressure widening is greatest at the intensity max. of the band for both P - and R -branches, in agreement with Cornell (A., 1937, I, 343). The mean widening increases \propto pressure. Widening produced by the addition of foreign gases (N_2 , N_2O , H_2S , Me_2O , SO_2 , $EtCl$) depends largely on the dipole moment of the added gas, other factors being equal. The widening is, however, not \propto dipole moment. The effect may be due to van der Waals forces and/or resonance.

A. J. M.

Asymmetric rotor. II. Calculation of dipole intensities and line classification. P. C. Cross, R. M. Hainer, and G. W. King (*J. Chem. Physics*, 1944, 12, 210–243; cf. A., 1943, I, 113).—Mathematical. Provided that the asymmetry is roughly the same in the initial and final states, the relative intensities of all important rotational lines up to $J < 13$ for all bands of any mol. can be calc. with the aid of a table of line strengths for rigid asymmetric rotors. Irregularly spaced lines are classified into "sub-branches," defined by the changes of the K vals. of the initial level in the limiting prolate and oblate symmetric rotors, and "wings" which collect lines of "sub-branches" which have uniformly varying strengths and Boltzmann factor, and fairly uniform spacing.

W. R. A.

Absorption spectra of complex compounds of the noble metals. Chlorometallates of the platinum group. A. V. Babaeva (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 171–177).—Absorption spectra have been studied in the region 2000–6000 Å. for dil. (0.001–0.03M.) aq. solutions of $(NH_4)_2[RhCl_5] \cdot H_2O$; $(NH_4)_2[PdCl_4] \cdot H_2O$; $(NH_4)_2[PtCl_4] \cdot H_2O$; $(NH_4)_2[PtCl_6] \cdot 6H_2O$. These compounds each have three absorption bands in the range studied, the positions of which are governed by the at. no. of the "central atom" of the complex.

V. B.

Photochemical processes in aromatic compounds.—See A., 1944, 235.

Polymer spectra of cyanine dye. R. W. Mattoon (*J. Chem. Physics*, 1944, 12, 268–276).—Dil. aq. solutions of 1:1'-diethyl-2:2'-cyanine chloride (I) exhibit bands with max. at 4900 and 5230 Å., whilst in a 10⁻³M. solution an exceedingly narrow absorption and fluorescence band occurs at 5730 Å. (P band) at room temp. The P band shifts to ~ 5780 Å., becomes broader, and finally disappears as H_2O is removed by pumping or by heat. The behaviour is reversible, thus enabling the humidity of the atm. to be determined from the position of the band. The effect of temp. from -195° to 100° has been investigated. For films of (I) another, and weaker, absorption band occurs at 5430 Å. (P_M band) similar to the P band but polarised perpendicular, not parallel, to the polymer chains. Thus the P band is due to single dye polymer chains and the P_M band to a system of coupled chains lying mutually parallel and forming threads. The threads were observed microscopically.

W. R. A.

Physico-chemical constants of cholesterol and its ozonide. H. Paillard, M. Berenstein, and E. Briner (*Arch. Sci. phys. nat.*, 1944, [v], 26, Suppl., 67–71).— d_4^{25} , n_D^{25} , γ^{18} , a , $[\alpha]_D$, and η for solutions of cholesterol (I) and of its ozonide (II) in CCl_4 and in $CHCl_3$ are recorded. The ultra-violet absorption of (II) is displaced towards longer λ and commences at 3400 Å. $CHCl_3$ solutions of (I) and (II) exhibit a weak greenish fluorescence; (I) has a single band at ~ 4700 –5300 Å. and (II) at 5000–6100 Å.

L. S. T.

Study of the structure and modes of vibration of metallic carbonates, hydrogen carbonates, and thiocarbonates by means of their infra-red absorption spectra. (Mme.) R. Duval, C. Duval, and J. Lecomte (*Bull. Soc. chim.*, 1943, [v], 10, 517–524).—The infra-red absorption spectra of 12 simple carbonates, 7 double carbonates, 5 H carbonates, and 5 thiocarbonates are obtained by the powder method. From the results, definite modes of vibration can be associated with all the observed frequencies, and a choice can be made between the various possible mol. models. Certain bands in the spectra of the thiocarbonates indicate the presence of acid thiocarbonates.

J. F. H.

Application of infra-red absorption spectra to the determination of the structure of ethylenic hydrocarbons (aliphatic series). M. Tuot and J. Lecomte (*Bull. Soc. chim.*, 1943, [v], 10, 524–542).—The infra-red absorption spectra of 22 ethylenic hydrocarbons, obtained by the dehydration of *sec.* and *tert.* alcohols, have been determined in the range 700–1400 cm^{-1} . The region 880–1000 cm^{-1} gives information on the position of the double linking. None of the dehydration products gives bands at 910 and 990 cm^{-1} , indicating that no $\alpha\beta$ ethylenic linkings are formed. A double linking not at the end of the chain gives strong bands at ~ 960 and 910 cm^{-1} , except where the double linking is attached to a *tert.* C, when a strong band appears at 880–890 cm^{-1} . Study of the region 720–780 cm^{-1} enables the length and form of the C chain to be deduced. The results are discussed theoretically.

J. F. H.

Empirical and theoretical considerations on the infra-red absorption spectra of saturated aliphatic secondary and tertiary alcohols. M. Tuot and J. Lecomte (*Bull. Soc. chim.*, 1943, [v], 10, 542–561).—The infra-red absorption spectra of 30 *sec.* and 20 *tert.* saturated aliphatic alcohols are examined in the range 6.5–15 μ . *sec.* Alcohols show a characteristic band at $\sim 9 \mu$, *tert.* alcohols at $\sim 8.75 \mu$. Chain-branching generally displaces the characteristic bands to lower λ and reduces the intensities of the absorption max. Consideration of mol. vibrations furnishes a theoretical explanation of the form of the spectra of the simple types; by analogy the treatment is extended to homologues.

J. F. H.

Infra-red spectrum of allene and interactions between molecular vibration and rotation. H. W. Thompson and G. P. Harris (*Trans. Faraday Soc.*, 1944, 40, 295–300).—The infra-red spectrum of allene vapour has been re-measured over the range 3–20 μ . The main conclusions of Linnett and Avery (A., 1939, I, 8) are substantiated, and the use of higher resolving power has revealed details which are discussed.

F. L. U.

Optical methods of studying hydrocarbons. III. Combination scattering spectra of paraffins. P. A. Bashulin, M. F. Bokshtein, A. L. Liberman, M. J. Lukina, E. I. Margolis, O. P. Solovova, and B. A. Kazanski (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 198–205).—Spectral data are given for the following hydrocarbons: $\beta\beta$ - and $\beta\gamma$ -dimethylbutane; $\beta\gamma$ -, $\beta\delta$ -, and $\gamma\gamma$ -dimethylpentane; $\beta\beta\gamma$ -trimethylbutane; $\beta\beta$ -, $\beta\gamma$ -, and $\gamma\delta$ -dimethylhexane; $\beta\beta\gamma$ - and $\beta\gamma\delta$ -trimethylpentane; β - and γ -methyl- γ -ethylpentane; $\beta\beta\gamma\gamma$ -tetramethylbutane; $\beta\gamma\gamma$ -trimethylpentane. Methods of prep. and the principal physical consts. are also given. Certain of the data previously given (*ibid.*, 1941, 14) are modified by more accurate standardisation of the lines for cyclohexane.

V. B.

Raman spectra of some trihalogen derivatives of methane. (Mlle.) M. L. Delvaule (*Compt. rend.*, 1943, 216, 735–737).—The Raman spectra of CH_2FCl , CH_2ClBr , and CH_2Br_2 have been reinvestigated. For CH_2FCl there are 10 lines (instead of 9) and for CH_2ClBr 11 lines are found, the most intense being a doublet in each case. For CH_2Br_2 , 9 lines are found. The λ and degree of polarisation of each line are given, and the results are discussed.

A. J. M.

Raman spectra of hexachloroethane and hexabromoethane. D. T. Hamilton and F. F. Cleveland (*J. Chem. Physics*, 1944, 12, 249—252).—Raman ν of C_2Cl_6 and C_2Br_6 , and their relative intensities and depolarisation factors, are given. The fundamental ν of C_2Cl_6 have been used to calculate force consts. using Stitt's equations for C_2H_6 . The equilibrium configuration corresponds with the point-group D_{3h} . ν allowed in the infra-red have been calc. Selection rules for the fundamentals, binary combinations, and overtones of degenerate and non-degenerate ν have been worked out for mols. having the symmetries D_{3h} , D_{3d} , and D_{3d} . W. R. A.

Reversible extinction of fluorescence of hæmatoporphyrin in solution. I. Ungar (*Anal. Asoc. Quím. Argentina*, 1942, 30, 217—219).—The fluorescence of 0.001% hæmatoporphyrin solution in a beam of an arc lamp filtered through 6% $CuSO_4$ is extinguished by 0.1% of $FeCl_3$. Addition of 1% of $Na_3P_2O_7$ causes reappearance of the fluorescence. It is concluded that the extinction is accompanied by a reduction of Fe^{+++} to Fe^{++} , which change is inhibited by $Na_3P_2O_7$. F. R. G.

Factors that alter the fluorescence of certain carcinogens. H. Weil-Malherbe (*Cancer Res.*, 1944, 4, 102—105).—The chemical classification of a solvent has no relation to the fluorescence intensity of hydrocarbons dissolved in it. With 3:4-benzpyrene (I) in $EtOH-H_2O$ mixtures the variation of fluorescence intensity with composition is entirely due to quenching by dissolved O_2 . The stability of the fluorescence of solutions of (I) depends on the solvent. In C_6H_{14} or C_6H_6 no change occurs during 20 min. irradiation. In $AcOH$ photo-oxidation occurs in presence of O_2 . In $EtOH$ and in $EtOH-H_2O$ mixtures, 0.1N-HCl, or 0.1N- $NaOH$ a slow non-oxidative fall in fluorescence occurs. The rapid destruction of fluorescence in $CHCl_3$ solution is non-oxidative. Inhibitors of fluorescence in solution are of three categories: (a) substances causing a reversible photochemical reaction; (b) substances causing irreversible changes of the fluorescent material; (c) substances that absorb the exciting λ . An unsaponifiable fraction of mouse tissues is less susceptible to the quenching effect of O_2 than are carcinogenic hydrocarbons. Fluorimetric determinations of hydrocarbons should be carried out in N_2 . F. L. W.

Hedvall wandering of disturbance centres. F. Moglich and R. Rompe (*Naturwiss.*, 1943, 31, 69).—A quantum-mechanical basis for diffusion of excess energy in a solid structure is suggested.

Fluorescence and absorption spectral data for pterin-like pigments synthesised by the diphtheria bacillus and isolated by chromatographic analysis.—See A., 1944, III, 772.

Dielectric properties of dipolar substances. H. Fröhlich and R. Sack (*Proc. Roy. Soc.*, 1944, A, 182, 388—403).—Examination of the structural evidence shows that there is a large group of dipolar org. solids the dipoles of which have two equilibrium positions with opposite dipole direction. A theory is developed which gives larger dielectric consts. and smaller dielectric loss than Onsager's theory. It is shown that liquids with high η behave as solids whilst liquids of low η conform to Onsager's theory. G. D. P.

Refraction and dispersion of hydrogen sulphide, sulphur dioxide, and carbon oxydisulphide. H. Huxley and H. Lowery (*Proc. Roy. Soc.*, 1943, A, 182, 207—216).—The measurements were carried out by means of Jamin's interferometer; an improved technique makes it possible to apply a systematic correction for fringe drift by obtaining photographic records of a fringe system at definite intervals during the experiment. New vals. for the refraction and dispersion of SO_2 and H_2S are given. For COS the following consts. are determined for the first time: pressure coeff. = 0.1339×10^{-4} per mm.; $\rho = 2.1046$ (air = 1); temp. coeff. = 0.003830 per $^\circ C$. Dispersion, $(n - 1) \times 10^7$, at eight Hg λ 's, from 8817.0 at $\lambda 5792.26$ to 9061.9 at $\lambda 4047.70$. The Sellmeier formula deduced from these figures is: $(n - 1) = 9.372 \times 10^{27} / (10,903 \times 10^{27} - \nu^2)$. G. D. P.

Transmission of light by water drops 1 to 5 μ . in diameter. R. Ruedy (*Canad. J. Res.*, 1944, 22, A, 53—66).—The work done against surface tension in the formation of a small H_2O drop from supersaturated vapour is large compared with hT . This prevents the attainment in cloud-chamber experiments of the equilibrium indicated by Kelvin's v.p. equation. The colours observed when a source of white light is viewed through a cloud of drops of radii of a few μ . are explained in terms of the theoretical result that the intensity of transmitted monochromatic light varies periodically as the ratio radius/ λ increases. H. J. W.

Old and new views on some chemical problems. W. H. Mills (*J.C.S.*, 1944, 340—350).—An address. Recent advances in the knowledge of mol. structure, especially in relation to valency, are reviewed. C. R. H.

Calculation of certain higher-order Bethe approximations. W. J. C. Orr (*Trans. Faraday Soc.*, 1944, 40, 306—320).—Mathematical. The Bethe method is applied in calculating the no. of ways of arranging double mols. on planar arrays of adsorption sites. When consistently applied the method gives an unambiguous and apparently rapidly convergent result. F. L. U.

Effect of polar and paramagnetic molecules on absorption and refraction of radio-waves in the atmosphere. V. L. Ginzburg (*Bull. Acad. Sci. U.R.S.S., Sér. Phys.*, 1943, 7, 96—98).—The effect of paramagnetic mols. is small, and that of polar mols. negligible. J. J. B.

Radius of the H^+ ion, and constitution of the halogen acids. H. Triché (*Compt. rend.*, 1943, 216, 737—739).—It is possible to calculate approx. the radius of ions from the parachors of a family of compounds, and a certain no. of ionic radii (*ibid.*, 641). The method is applied to HCl, HBr, and HI. From the mean of the parachors of HCl and HBr, the radius of H^+ is 1.27 Å, and from HBr and HI it is 1.46 Å. The radius of H^+ is thus not small, and in the halogen acids the halogen ion must have a very small radius, but may be regarded as expanding to a vol. equal to the part of the H^+ which it encloses. The method is also applied to NH_3 , PH_3 , and AsH_3 , the radius of H^+ being 1.44—1.56 Å. A. J. M.

Molecular volume and structure. VII, VIII. T. W. Gibling (*J.C.S.*, 1944, 380—383, 383—385).—VII. The parachor vals. allotted (A., 1941, I, 324) for (C)·CO(C) and (C)·CHO should be increased by 0.1. "Standard vals." of compounds containing these groupings require additions of 0.1 or 0.2 unit. The correction for the δ -C in the O chain of aliphatic esters and ethers is —0.7. Modified vals. of previous data are given for *cyclo*-paraffins and -olefins and their derivatives.

VIII. Group vals. are estimated from published parachor data for alkyl sulphides, thiols, and disulphides. Interference corrections required in parachors of Hg *n*-alkyl mercaptides suggest a zig-zag arrangement of alkyl chains on opposite sides of the S-Hg-S nucleus in the liquid state. Alkyl sulphites have structures resembling those of the carbonates, and sulphates and phosphates also appear to belong to the same type. L. J. J.

Mol. wt. of cellulose. Average degree of polymerisation.—See A., 1944, II, 327.

Steric inhibition of resonance. I. Dichloronitrobenzenes. II. *m*-Xylidines and *N*-dimethyl-*m*-xylidines. G. Thomson (*J.C.S.*, 1944, 404—408, 408—410).—I. Mol. solution vols. and mol. refractivities of the 6 isomeric $C_6H_3Cl_2NO_2$ have been measured. The 2:6-compound has appreciably greater vals. for mol. solution vol., parachor, and energy of activation for reaction with NaOMe and smaller mol. refractivities for NaD and Hg_{6441} lines. The effect is attributed to inhibition of resonance between the $\cdot NO_2$ and the C_6H_5 nucleus.

II. At. refractivity of N in 1:3:2- $C_6H_3Me_2NMe_2$ (I) is approx. the val. in aliphatic tertiary amines, whilst in the 1:3:4-compound (II) it has the normal aromatic val. With Me *ortho* to the NMe_2 group an intermediate val. is found. The mol. solution vol. of (I) is > that of the 1:3:5-compound (III) but approx. that of (II). The parachor vals. are in the order (III) > (II) > (I). L. J. J.

Form and mobility of thread molecules in experiments with models. H. A. Stuart (*Naturwiss.*, 1943, 31, 123—127).—Models of thread mols. were shaken in an empty vessel, and in a vessel filled with glass beads to represent an indifferent solvent. Photographs of the statistical forms taken up by mols. of different lengths are given. The effect of solvation is also shown. The transition from dil. to conc. solution is accompanied by parallelism of mols. A. J. M.

III.—CRYSTAL STRUCTURE.

Use of the X-ray goniometer (differential X-ray goniometer). W. Hofmann (*Naturwiss.*, 1943, 31, 113—114).—An arbitrary axis of rotation of the crystal can be used if two photographs are taken, one a normal rotation photograph with stationary film, the other with half the film obscured and the rotation of the crystal coupled with longitudinal displacement of the film cylinder. L. J. J.

Calculation of density from X-ray data. W. G. Schlecht (*Amer. Min.*, 1944, 29, 108—110).—The val. of N to be selected for calculating ρ from X-ray measurements is discussed. L. S. T.

Improved algebraic method for the determination of crystal structure from X-ray data. S. H. Yu (*Sci. Rec. [Acad. Sinica]*, 1942, 1, 109—110).—Avrami's method consists in solving an algebraic equation of degree $n = m(m - 1)$, where m is the no. of x , y , or z components of the interat. distances to be determined. The present method is an improvement in that (i) it is necessary only to solve an equation (determinantal) of degree $n/2$ and (ii) the no. of terms needed in a given spectrum $H(h,k,l)$ is reduced from $2n$ to $n/2 + 1$. Hence intensity data of very high-order reflexions are not needed so that some experimental difficulties are avoided. L. S. G.

New method of analysis of X-ray data for the determination of crystal structure; its application to iron pyrites. S. H. Yu and C. P. Ho (*Sci. Rec. [Acad. Sinica]*, 1942, 1, 111—115).—A modification of the Patterson synthesis is developed and compared with the latter in an application to the analysis of the structure of Fe pyrites. The rates of convergence of the two methods are discussed and also the resolving power between peaks on the Patterson

diagram. It is claimed that the new method is much more powerful than the classical Patterson method.

L. S. G.

Application of the micro-absorption factor to problems of lattice distortion and the nature of anti-phase domains. A. Taylor (*Phil. Mag.*, 1944, [vii], 35, 404—414).—The results of Brindley and Spiers (A., 1936, 3) for the differences between the f -factors of chemically pptd. and filed metal powders are explained in terms of the micro-absorption factors of the powders, that of the ppt. being larger. An experimental procedure is suggested for testing the hypothesis that the broadening of the superlattice lines in the Debye-Scherrer spectrum of Cu_3Au is due to the existence of ordered domains or to lattice faults in the crystallites.

H. J. W.

Isotypism and isomorphism. F. Machatschki (*Naturwiss.*, 1943, 31, 43).—A reply to a criticism by Strunz (cf. A., 1943, I, 221) of the use of the phrase "isomorphism of elements." The new term "diadochism," proposed by Strunz, is unnecessary. The idea of "coupled diadochism," and the distinction between isotypism and isomorphism, are criticised.

A. J. M.

Isotypism and isomorphism. H. Strunz (*Naturwiss.*, 1943, 31, 93—94).—A reply to Machatschki (see preceding abstract).

L. J. J.

Matrix theory of correlations in a lattice. I, II. R. Eisenschitz (*Proc. Roy. Soc.*, 1944, A, 182, 244—259, 260—269).—I. The statistical mechanics of some cryst. systems may be reduced to statistical correlations between objects which are the unit cells of a fictitious lattice. The method leads to the definition of matrices such that the probability distribution for a chain of cells is found by forming the powers of a matrix. A similar approach to the statistics of a lattice involves infinite matrices. In certain conditions the infinite matrices may be replaced by the outer power of finite matrices. An equation is given for the thermodynamic energy as a function of temp.

II. The sp. heat-temp. curve for order-disorder equilibrium is derived from the nearest-neighbour model by means of the above theory. The calc. curve bears very little resemblance to the experimental.

G. D. P.

Asymptotic formulæ relating to the physical theory of crystals. W. Ledermann (*Proc. Roy. Soc.*, 1944, A, 182, 362—377).—The validity of certain approximations which had been used in the mathematical theory of crystals having been questioned, a rigorous examination of the problem was undertaken. The old procedure is fully justified provided that the no. of boundary particles is small compared with the total no. of particles in the crystal. Lattice sums may be replaced by infinite series and the distribution of frequencies closely follows Born's law for cyclic crystals. Upper limits are obtained for the errors caused by such approximations.

G. D. P.

Analysis of intracrystalline forces in simple layer lattices. I. Electrostatic energy and the Madelung constant. Z. G. Pinsker (*Acta Physicochim. U.R.S.S.*, 1943, 18, 311—324).—Mathematical. The Madelung const. have been calc. for the CdI_2 , CdCl_2 , and CdBr_2 lattices according to Borzoth, and for the CdI_2 lattice according to Hassel. The electrostatic energies calc. from these const. are compared with the total lattice energies as determined by the Born-Haber cycle. The electrostatic energy and the % of electrostatic to total energy decrease in the order $\text{CdCl}_2 > \text{CdBr}_2 > \text{CdI}_2$.

C. R. H.

Structure of electro-deposited chromium. W. Hume-Rothery and M. R. J. Wyllie (*Proc. Roy. Soc.*, 1944, A, 182, 415).—A correction (cf. A., 1944, I, 53).

G. D. P.

Crystal structures of LaMg_2 and CeMg_2 . F. Laves (*Naturwiss.*, 1943, 31, 96).— LaMg_2 and CeMg_2 crystallise in the MgCu_2 type with lattice const. $a = 8.77 \pm 0.01$ and 8.71 ± 0.01 Å, respectively.

L. J. J.

Crystal structures of CaGa_2 , LaGa_2 , and CeGa_2 . F. Laves (*Naturwiss.*, 1943, 31, 145).— CaGa_2 has a 4.314, c 4.314 Å. LaGa_2 has a 4.320, c 4.396 Å. CeGa_2 has a 4.303, c 4.307 Å. Co-ordination nos. 12 and 6. Structural type is that of AlB_2 .

A. J. M.

High-temperature modification of sodium nitrite. B. Strijk and C. H. MacGillivray (*Rec. trav. chim.*, 1943, 62, 705—712).— NaNO_2 , orthorhombic and hemihedral at room temp., shows an anomaly in the temp. variation of the cell dimensions at 158° . Powder diagrams show the crystals to remain orthorhombic and body-centred but the intensities of reflexion are changed; trial analysis shows the crystal to have assumed a centrosymmetrical structure. The piezo-electric effect disappears completely at 160° . The Na—O distance is hardly changed by the modification but the distances in the NO_2 group are extended and the N bond angle becomes smaller. Comparison with data for N_2O_4 and MeNO_2 shows angles for the N—O bonds in accord with those of the low-temp. form and the N—O distances midway between those for the two forms.

J. O'M-B.

Crystal structure of sodium and ammonium iodate. C. H. MacGillivray and C. L. Panthaleon van Eck (*Rec. trav. chim.*, 1943, 62, 729—735).—Single crystals were obtained by evaporation from saturated solution at 100° . For NaIO_3 , described by Zachariassen

as an antiperovskite (A., 1929, 1131), the axial ratios agree with those of Eakle (A., 1897, ii, 21). The cell const., determined by Weissenberg diagrams, show a and b in agreement with the vals. of Zachariassen (*loc. cit.*), but c twice as great. The unit cell contains 4 mols. of NaIO_3 and has orthorhombic symmetry. Space-group D_{2h}^{10} — $Pbmm$. The position found for the Na agrees with that assigned by Zachariassen but that of I must be modified to agree with the new length of the c axis. Evidence is given that the I atom contributes to reflexions hkl with odd l , from which the x and y parameters of I on $4c$ are >0 . A possible configuration for O is derived from Goldschmidt's ionic radii; the trial analysis is confirmed by Fourier synthesis. The lattice has a co-ordination structure of Na and IO_3 ions in deformed CsCl packing, the IO_3 ions having pyramidal shape. For NH_4IO_3 , previously described as a perovskite (A., 1926, 228), the conclusions are essentially the same. The crystals used were tetragonal twins; since reflexions hkl and $h\bar{k}l$ overlap almost completely it is difficult to determine the space-group, which is probably $Pbmm$.

J. O'M-B.

Space-groups of $\text{NiCl}_2 \cdot 6\text{NH}_3$, $\text{NiBr}_2 \cdot 6\text{NH}_3$, and $\text{NiI}_2 \cdot 6\text{NH}_3$. S. H. Yu (*Sci. Rec. [Acad. Sinica]*, 1942, 1, 151).—It was formerly thought that crystals of these salts must have the symmetry of one of the space-groups $Fm3$ (T_h^1), $F43$ (O_h^3), and $Fm3m$ (O_h^5). Reasons are adduced for concluding that the correct space-group is $F43m$.

L. S. G.

Structure of rhodizite. H. Strunz (*Naturwiss.*, 1943, 31, 68).—Rhodizite, $\text{KNaLi}_4\text{Al}_4\text{B}_6\text{O}_{27}$, has T_h^1 — P_{432} symmetry, with a_0 7.30 Å. and $Z = 1$. The co-ordination nos. of Li and Al are 6, for (K, Na) 12, and for (B, Be) 4, for O.

L. J. J.

Low-chalcocite and high-chalcocite.—See A., 1944, I, 259.

Chemistry of oriented growth of crystals of organic substances. J. Willems (*Naturwiss.*, 1943, 31, 146—147).—Oriented growth of org. substances takes place when mol. linkings connect the lattice of the crystallising compound with that of the substrate. In this connexion the following types of mol. compound are distinguished: (1) $\text{MSO}_4 \cdot n\text{H}_2\text{O} \cdot (\text{CH}_2)_n\text{N}_4$, exemplified by the oriented growth of $(\text{CH}_2)_6\text{N}_4$ from C_6H_6 solution on (010) of gypsum; (2) quinone-metallic halide, exemplified by the oriented growth of 1:4-naphthaquinone, anthraquinone, and 1:4:6-trichloroanthraquinone from C_6H_6 solution on (100) of alkali halides. The growth of naphthazarin on (100) of an alkali halide also belongs to this class; (3) picric acid-aromatic hydrocarbon, exemplified by the growth of coronene from decalin solution on (010) of picric acid.

A. J. M.

Order-disorder transformations in the lattice of organic molecules.

II. **Crystal structure of tetramethyl orthothiocarbonat below 23.2° .** W. G. Perdok and P. Terpstra (*Rec. trav. chim.*, 1943, 62, 687—695).— $\text{C}(\text{SMe})_4$ has singular physical properties (*ibid.*, 1942, 61, 533). Rotational photographs resemble powder diagrams owing to the transition point at 23.2° , at which temp. the original tetragonal crystals become conglomerates of very small crystals. a 8.536 ± 0.002 , c 6.949 ± 0.002 Å. (temp. = 18°), ρ 1.321; two mols. per unit cell. Space-group D_{2d}^4 ($P4_2/c$). The observed piezo-electric effect disappears as expected on heating above 23.2° . Bragg synthesis shows the c axis to be most closely occupied by atoms; this explains the tendency to crystallise in needles stretched along a tetragonal axis, which possesses smaller energy. The SMe groups are arranged tetrahedrally around the C atoms with C—S = 1.81 Å. and the Me groups in a pattern resembling a body-centred lattice, the interstices of which are alternately empty or filled with CS_2 groups.

J. O'M-B.

Form and mobility of cellulose molecule. P. H. Hermans, J. de Booy, and C. J. Maan (*Kolloid-Z.*, 1943, 102, 169—180).—Using commonly accepted vals. for at. distances, valency angles, and effective radii of atoms, the configuration of the straight cellulose chain is calc. The packing of parallel chains is considered. In order to make the length of the cellobiose radical agree with the identity period determined by X-ray methods, it must be assumed that the chain takes up a bent position, and the rings of successive glucose groups do not lie exactly parallel to each other. The model proposed does not differ greatly from that formerly deduced from X-ray data. The packing of several straight and parallel chains can be brought into agreement with X-ray data only when the chains have alternating polarities in successive layers in the direction of the c -axis. The chains in successive layers must also be displaced in the direction of the thread axis by ~ 3 —4 Å. The chain can change comparatively easily into a more or less crumpled or ball-like form.

A. J. M.

Small-angle interferences in myosin. O. Kratky, A. Sekora, and H. H. Weber (*Naturwiss.*, 1943, 31, 91).—Three weak equatorial reflexions corresponding with lattice plane separations of 33, 42, and 66 Å. are found in myosin threads, corresponding with the electron-microscope val. 50—60 Å. for the thread thickness. A further 100 Å. dimension may correspond with micellar widths.

L. J. J.

Small-angle interference of myosin.—See A., 1944, III, 764.

Magnesium oxide crystals in the electron microscope. E. Kinder (*Naturwiss.*, 1943, 31, 149).— MgO crystals obtained by burning

Mg have been examined with the electron microscope. Bright and dark stripes parallel to the cube edges are observed. In any one crystal the stripes are equidistant, ~ 16 – 20 μ . apart, and all crystals on a given photograph have stripes the same distance apart. To obtain the stripes the electron beam must be at a definite inclination to the cube edges. A. J. M.

Electron microscope photographs of fine reaction films on crystals of metallic oxide smokes. M. von Ardenne and D. Beischer (*Kolloid-Z.*, 1943, 102, 127–131).—The film-like structure of the product obtained by burning Mg in air is a reaction film of basic MgCO_3 . The photograph of freshly deposited MgO shows two types of particle, one with an edge of ~ 100 – 550 \AA ., and the other consisting of larger crystallites with an edge of ~ 0.5 μ . The latter are formed by the heterogeneous reaction of the aerosol with H_2O and CO_2 . If the freshly deposited MgO is kept for several hr. in contact with air containing H_2O and CO_2 , the small particles become surrounded with a reaction layer of basic MgCO_3 . In this process the d falls from 3.58 to 2.32. Similar reaction layers on ZnO particles could not be ascribed to reaction between the smoke and CO_2 or NH_3 . They are probably due to impurities in the original Zn. A. J. M.

Photodichroism of coloured laminæ of potassium chloride. S. Nikitine (*Compt. rend.*, 1943, 216, 730–732).—Photodichroism is observed with thin coloured sheets of KCl, as with NaCl (A., 1942, I, 260). Unlike NaCl, reheated coloured crystals of KCl are unstable, and become spontaneously decolorised in the dark. The extinction curve of the coloured sheet before irradiation with polarised light, the curve of variation of photodichroism as a function of λ , and a similar curve after keeping the sheet for 3 hr. in darkness, are given. The last two curves differ markedly from the corresponding ones for NaCl. Two types of transformation can occur in coloured crystals: (i) the disappearance of F and F' centres (decolorisation) and (ii) the transformation of an F into an F' centre, or the reverse. The more important is (ii) with NaCl and (i) with KCl. A negative photodichroism curve is therefore obtained throughout the spectrum. A high proportion of F' centres exists with F centres in the coloured crystal after irradiation with X-rays. The F' centres are more important than F centres as regards photodichroism, and this causes displacement of the max. of the photodichroism curve to longer λ compared with the extinction curve. A. J. M.

Demonstration of positive or negative character of extremely small double refraction effects. F. Laves and T. Ernst (*Naturwiss.*, 1943, 31, 68–69).—The colour changes shown by a gypsum film between crossed Nicols on the introduction of a doubly-refracting crystal, and used to detect the positive or negative character of the birefringence, are much greater when the plane of vibration of the film is nearly parallel with that of the polariser ("sub-parallel" position) than in the usual arrangement when it is intermediate between those of polariser and analyser. The most favourable arrangement for use with very small degrees of birefringence is described. L. J. J.

Disperse structure of solid systems and its thermodynamic basis. XIII. D. Balarew (*Kolloid-Z.*, 1943, 103, 221–228).—Further evidence for the author's theory is derived from observations on the effect of appropriate heat-treatment on the rate of reaction between Ag and I vapour, the colour of Au–Ag alloys and of KCl–KBr mixed crystals, the swelling of cruciform BaSO_4 crystals, and the adsorption capacity of CaF_2 gels for certain dyes. Other phenomena bearing on the theory are also considered. R. H. F.

New phenomenon in the piezo-electric oscillations of a quartz crystal. S. Parthasarathy, A. Pande, and M. Pancholy (*J. Sci. Ind. Res. India*, 1944, 2, 295–296).—An X-cut quartz crystal of fundamental frequency ~ 580 kc. per sec. was excited by a 40-w. Hartley parallel-feed circuit, and the diffraction patterns obtained with a Hg 5461- \AA . source were photographed. Under suitable excitation conditions it is possible to make the crystal vibrate, not only at odd harmonics, but also at even and half-of-odd harmonics. The odd and half-of-odd harmonics could be excited to 3 or 4 orders, whereas even harmonics could be excited to ≥ 2 orders. J. G.

Internal stress created by plastic flow in mild steel, and stress-strain curves for the atomic lattice of higher carbon steels. S. L. Smith and W. A. Wood (*Proc. Roy. Soc.*, 1944, A, 182, 404–414; cf. A., 1941, I, 167; 1942, I, 261; B., 1943, I, 122).—The stresses remaining in a specimen after permanent deformation are measured by observation of the residual lattice strains. Mild steel after subjection to tension exhibits a longitudinal compression and lateral expansion in the ratio 2:1. The density thus remains unchanged. Comparison of X-ray and mechanical measurements shows that the elastic hysteresis loop of mild steel after overstrain can disappear and the linear elastic relation be recovered without change in the internal stress, which is therefore a more fundamental physical property. When the elastic range is extended by overstrain in tension there is no symmetrical increase in the elastic range in subsequent compression. Comparisons of the lattice stress-strain curves of 0.4% C steel (partly pearlitic) and of 0.8% C steel (pearlitic) with those of pure Fe and 0.1% C steel (annealed) show that

the max. residual internal strain developed by a lattice increases markedly with the fineness to which the crystallites can be broken down by plastic deformation. G. D. P.

Explanation of the observations of Stranski and Suhrmann on the melting of single-crystal tungsten wires. J. Leonhardt (*Naturwiss.*, 1943, 31, 139–140; cf. A., 1943, I, 147).—If a W single-crystal wire is corroded, either chemically or by evaporation on heating, the (011) surface forms corrosion furrows without slip surfaces. If a deformed single crystal is corroded, slip surfaces are shown on (211). The mechanism of the fusion of such wires is discussed on this basis. A. J. M.

Melting of single-crystal tungsten wires. I. N. Stranski and R. Suhrmann (*Naturwiss.*, 1943, 31, 140).—A reply to Leonhardt (see preceding abstract). A. J. M.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

The intermediate state between normal conductivity and superconductivity. K. M. Koch (*Kolloid-Z.*, 1943, 105, 89–97).—A theory of transition from normal conductivity to superconductivity is given. At normal temp. a metal consists of two types of atom which differ in their electron shells (cf. dia- and para-magnetic atoms). Those corresponding to diamagnetic (I) are responsible for conductivity, and as the superconducting state is approached, both types coalesce into micro-regions having the properties of (I). At and before the transition point these form a "superstructure" similar to a macromol., and analogous to the order-disorder transition in Cu–Zn and Cu–Au systems. The behaviour of superconducting hollow bodies in a magnetic field, certain hysteresis phenomena in the transition from normal conductivity to superconductivity, and the Meissner-Ochsenfeld effect are explained by the theory. J. H. BA.

Magnetic properties of nickel supersaturated with carbon. W. Gerlach and J. von Rennenkampff (*Naturwiss.*, 1943, 31, 96).—The temp.–magnetisation relation of Ni supersaturated with C is anomalous only between room temp. and 300° , and not at -200° to 0° . The coercivity decreases normally from -200° to $\sim 50^\circ$ and then remains const. up to $>300^\circ$. In the anomalous region of the temp.–saturation curve, saturation is not reached at 3000 oersted, suggesting the existence of numerous Curie points. The remanence increases below 0° . Lange's Ni–C alloy consists of a definite ferromagnetic substance with Curie temp. $\sim 50^\circ$ and a no. of other ferromagnetic alloys. L. J. J.

Physical properties of aliphatic compounds. A. W. Schmidt (*Ber.*, 1942, 75, [B], 1399–1424).—M.p., d , and n_D^{20} for a lengthy series of n -paraffins, Δ^a -olefines, n -alkylcyclo-pentanes and -pentenes, n -alkyl-benzenes and -cyclohexanes, and isoparaffins are discussed. Graphs are plotted and their usefulness in confirming the experimental results, particularly those obtained at low temp., is stressed. Only when the observation falls on the graph for the homologous series can the individual result be accepted without reserve since the physical consts. are very subject to the influence of relatively small amounts of impurity which evade detection by the usual tests. H. W.

Specific heat of metals crystallising in the cubic system. B. Dayal (*Proc. Indian Acad. Sci.*, 1944, 20, A, 24–50).—Sp. heat data for Al, Ag, Au, Cu, and Pb (face-centred), Li, K, Na, and W (body-centred) crystals have been evaluated by Raman dynamics of crystal lattice from known elastic consts. and a Debye function representing the other degrees of freedom. Calc. and experimental vals. are in fair agreement. The accuracy with which sp. heat data can be represented by a single Debye function is discussed. W. R. A.

Some properties of non-oxidisable invar. C. Volet and A. Bon-houré (*Compt. rend.*, 1943, 216, 734–735).—An alloy of 37% Fe, 54% Co, and 9% Cr has a lower coeff. of expansion than the usual Ni-steel invar. It is practically non-oxidisable, and is very stable. Its Young's modulus is $\sim 18,200$ kg. per sq. mm. When a bar of this material is made into wire the coeff. of expansion increases from 0.7×10^{-8} to 8.2×10^{-8} , whereas with Ni-steel invar there is a decrease. The effect of annealing on the hammered metal has been investigated. A. J. M.

Explanation of striking expansion phenomena with silica glass and special glasses. A. Dietzel (*Naturwiss.*, 1943, 31, 22–23).—The mean coeff. of expansion of SiO_2 glass above 400° decreases, and at higher temp. becomes negative. The max. val. is at 250° . If SiO_2 is fused with TiO_2 , a glass is obtained which has an even smaller coeff. than SiO_2 glass. If Al_2O_3 is fused with SiO_2 , the coeff. of the latter is almost unchanged. It is possible to explain this in two ways. If SiO_2 can be supposed to be made up of SiO_2 mols. which have polymerised into large aggregates, the introduction of Ti^{4+} or other strong cations, such as Al^{3+} , would link the SiO_2 mols. more firmly than the latter would bind themselves. Alternatively it may be supposed that fused SiO_2 has mixed ionic-at. linkings, being made up of a tetrahedral arrangement of Si^{4+} ions and O^{2-} ions and of SiO_2 dipoles. The strong Si^{4+} would cause such a glass

to have a low coeff. of expansion. If such a mixture were heated the equilibrium would move in favour of the ionic linking, and the Si—O distance would increase with rising temp. The increase of $[\text{Si}^{4+}]$ would, however, provide a stronger structure, and a lowering of the coeff. of expansion with increasing temp. (See also below.)

Thermodynamic properties of ethylene. R. York, jun., and E. F. White, jun. (*Trans. Amer. Inst. Chem. Eng.*, 1944, 40, 227—250).—A pressure-enthalpy-entropy diagram is constructed from known data for the range -140°F . to 500°F . and 1 to 300 atm.

Green's functions in the theory of heat conduction. A. N. Lowan (*Phil. Mag.*, 1944, [vii], 35, 495—498).—By superposition of solutions of the equation of heat conduction corresponding to sources and sinks, Green's functions are constructed for domains bounded by lines or planes which either are kept at 0° or are impervious to heat.

Effect of transverse high-frequency electric field on the viscosity of liquids. B. N. Singh and S. Ghose (*Indian J. Physics*, 1943, 17, 252—256).—An apparatus is described by means of which high-frequency fields of $\sim 10^4$ cycles per sec. can be applied transversely to liquids of fairly low conductivity flowing through narrow channels. The times of flow of xylene, $\text{C}_3\text{H}_7\text{OH}$, and EtOAc are unaffected by the field.

Initial deformations of flow [of metals]. J. de Lacombe (*Compt. rend.*, 1943, 216, 739—741).—The formula $\epsilon = \epsilon_0 + at^m + bt^n$, although it represents exactly the flow curves of metals over a long period, does not give the correct initial deformation when extrapolated and compared with the curve obtained when flow takes place more rapidly, ϵ_0 being $>$ the elastic deformation ϵ_e . The expression should be $\epsilon = \epsilon_e + \epsilon_p + at^m + bt^n$, ϵ_p being a function of time, rapidly reaching a limiting val. The effect of time, load, and temp. on ϵ_p has been investigated for a C-steel of medium hardness. The ϵ_p term corresponds to a very high initial speed of flow, and reaches its limit in ~ 30 min. Increase of load causes the limiting val. of ϵ_p to increase rapidly. The limiting val. increases with temp.

Internal friction of an α -brass crystal. C. Zener (*Amer. Inst. Min. Met. Eng.*, 1942, *Tech. Publ.* 1505, 5 pp.; *Metals Tech.*, 9, No. 6).—Internal friction measured in a single brass crystal at 620 and 1710 cycles per sec. at temp. between 330° and 550° rose rapidly to a max. at 420° and fell equally rapidly thereafter. This was considered to be due to inhomogeneities of unknown type giving rise to stress relaxation.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Viscosity and vapour pressure of dilute solutions. I. Introduction. H. G. de Carvalho (*Anais Assoc. Quim. Brasil*, 1944, 3, 31—36).—A survey of the formulæ which have been proposed for η of dil. solutions.

Relative viscosity of some aqueous solutions of sulphamic acid and of some of its salts at 25° . A. F. Schmelzle and J. E. Westfall (*J. Physical Chem.*, 1944, 48, 165—168).—The relative η and d of aq. solutions of $\text{NH}_2\text{SO}_3\text{H}$ and of its NH_4 , Ba, Ca, and Mg salts have been determined at 25° . The Jones and Dole fluidity equation, $(\phi - 1)/\sqrt{C} = A + B\sqrt{C}$ where ϕ = fluidity, C = concn. in g.-equiv. per l., and A and B are consts., is applicable for $C > 1$, whilst the Root equation, $(d - d_0)/C - k_1 + k_2\sqrt{C}$ where d_0 is the d for H_2O , and k_1 and k_2 are consts., is applicable for the entire concn. range.

Diffusion constant and particle size of the saponin of the white soapwort (sapoalbin). E. O. K. Verstraete and I. Grassmann (*Kolloid-Z.*, 1943, 195, 114—118).—The diffusion const. (D) and particle radius (r) of sapoalbin in H_2O , 28.8% and 48% aq. EtOH were determined by the interference method of Rogener (cf. A., 1943, I, 224). r is of the same order ($\sim 8.3 \text{ \AA}$.) in each solution, this val. indicating almost mol. particles. The small influence of EtOH on r is in agreement with earlier measurements on flocculation etc. The vals. of D obtained show considerable variation.

Method of growing single crystals of sodium stearate and sodium palmitate. A. de Bretteville, jun., and F. V. Ryer (*J. Physical Chem.*, 1944, 48, 154—158).—Na stearate can be crystallised only at a crit. concn. $<$ the gel point in 95% EtOH . Na palmitate does not crystallise below the gel point; crystallisation is induced by addition of some NaCl.

Structure of silicate glasses. A. Dietzel (*Naturwiss.*, 1943, 31, 110—112).—Solubility data in H_2O and 0.1N-HCl, density at 20° , and expansion between 20° and the transition temp. and thence to 1400° have been determined for Li, Na, and K silicate glasses with 15—30 mol.-% R_2O . The solubility increases in the order $\text{Li} < \text{Na} < \text{K}$, in each case increasing very slowly with alkali content up to 20 mol.-% for K and 30 mol.-% for Na, thereafter increasing rapidly. Density vals. show that Li is completely absorbed in the voids of the SiO_2 structure, Na' up to 70%, and K' up to 27%,

for the $\text{R}_2\text{O} \cdot 3\text{SiO}_2$ glass. Expansion up to the transition region increases in the order $\text{Li} < \text{Na} < \text{K}$. Expansion between the transition region and 1400° increases with alkali content up to 20 mol.-% for K and 25 mol.-% for Na, thereafter remaining const.; with Li it continues to increase up to 32%. Possible arrangements of cations in the interstices of the SiO_2 lattice are discussed.

Constitution of the system indium-zinc. F. N. Rhines and A. H. Grobe (*Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1682, 10 pp.; *Met. Tech.*, 11, No. 2).—Solidus and liquidus curves have been redetermined. There is a eutectic at 143.5° with 2.8% of Zn. The max. solubility of Zn in In is 1.2% and of In in Zn, 0.2%. The true compressive strength required to compress to a strain of 10% increases regularly with [Zn] but shows a slight unexplained max. at 3.48% of Zn.

Rolled zinc-titanium alloys. E. A. Anderson, E. J. Boyle, and P. W. Ramsey (*Amer. Inst. Min. Met. Eng.*, 1944, *Tech. Publ.* 1687, 9 pp.; *Met. Tech.*, 11, No. 2).—The Zn-Ti eutectic occurs with 0.12% of Ti (not 0.46% as hitherto reported) at 418.5° and the solid solubility of Ti in Zn is 0.007—0.015% at 300° . Addition of 0.05—0.23% of Ti to Zn causes grain refinement and increases the creep-resistance of hot-rolled strip. The 0.012% Ti alloy was found to soften when cold-worked and the creep-resistance was considerably impaired. The creep strength was, however, largely improved by annealing at 200 — 275° .

Dissociation of an alloy of copper, iron, and nickel. Further X-ray work. (Miss) V. Daniel and H. Lipson (*Proc. Roy. Soc.*, 1944, A, 182, 378—387).—The dissociation of the alloy Cu_2FeNi_3 was studied by means of the variation of intensity of the satellites which accompany the X-ray reflexions. It is shown that within the lattice there is a periodic variation of parameter due to variation of concn. The λ of the periodicity is $\sim 10^{-6}$ cm. The bearing of the observations on the kinetics of phase change is discussed.

Physico-chemical investigation of phases having a nickel arsenide structure in the systems iron-antimony-nickel and iron-antimony-cobalt. N. V. Ageev and E. S. Makarov (*Bull. Acad. Sci. U.R.S.S. Cl. Sci. Chim.*, 1943, 161—170).—Examination of the Fe-Sb-Ni and Fe-Sb-Co systems shows that in each there exists an uninterrupted series of solid solutions, of the Ni arsenide type, between the Ni-Sb and Fe-Sb and the Fe-Sb and Co-Sb binary systems respectively. A study of the micro-structure, electrical resistivity and its temp. coeff., and of the lattice consts. has enabled the ternary phases of the Ni arsenide type to be delimited.

Chemistry of alloys of transition metals. H. J. Wallbaum (*Naturwiss.*, 1943, 31, 91—92).—The formation of intermetallic compounds A_2B , where A is Ni, Cu, Zn, Ga, Al, Pd, Pt, or Au, and B is Ti, Zr, Nb, or Ta, is explained by the incompleteness of the $3d$ electron shell in Ni and neighbouring elements and the corresponding electronic conditions in the other transition elements forming such compounds.

Alloys of platinum and palladium.—See B., 1944, I, 340.

Accumulation of sulphur dioxide by sodium phosphate solutions. G. P. Lutschinski and R. M. Tavrovskaja (*J. Appl. Chem. Russ.*, 1940, 13, 421—427).—Solubility of SO_2 in Na_2HPO_4 solutions at 20° and at the b.p. is determined. At 20° it increases linearly with $[\text{Na}_2\text{HPO}_4]$; an 18% solution of Na_2HPO_4 dissolves 12% of SO_2 at 80 mm. Hg of SO_2 . Na_2HPO_4 solutions can be used for absorbing dil. SO_2 gas.

Critical solution temperatures of paraffins with nitrobenzene and $\beta\beta'$ -dichloroethyl ether. H. M. Woodburn, K. Smith, and H. Tetewsky (*Ind. Eng. Chem.*, 1944, 36, 588—590).—For n -paraffins in which the no. of C atoms gradually increases the difference between crit. solution temp. and NH_4Ph point gradually increases for PhNO_2 and gradually decreases for $(\text{Cl}[\text{CH}_2]_2)_2\text{O}$.

Gas absorption by a drop of liquid. K. Schabalin (*J. Appl. Chem. Russ.*, 1940, 13, 412—420).—When drops of H_2O fall in a tube the lower part of which is filled with NH_3 or CO_2 , and collect under a pool of oil at the bottom of the tube, the amount of NH_3 or CO_2 absorbed increases with the length (5—200 cm.) of the passage through NH_3 or CO_2 gas, but a large fraction of it is apparently due to adsorption during the impact of drops on the oil pool. The final concn. of NH_3 or CO_2 in the drop is the larger the smaller are the drops (0.2—0.4 cm.). The rate of absorption is affected by convection currents within the drop.

Measurements of activated adsorption by nickel films between 200° and 500° . A. van Itterbeck, P. Mariens, and O. van Paemel (*Ann. Physique*, 1943, [xi], 18, 135—144).—Activated adsorption of H_2 and D_2 , in contrast with low-temp. van der Waals adsorption, was investigated. Adsorption isobars obtained from measurements with a special apparatus are given, and anomalies in the neighbourhood of the Curie point are discussed in relation to available data and theories.

Process for determining absolute "occupation numbers" of molecules adsorbed from liquid mixtures on defined metal surfaces.

H. Harms (*Kolloid-Z.*, 1943, 103, 202—210).—Apparatus is described for determining the change in composition of a solution when one component is adsorbed on the surface of small falling drops of Hg. These are produced by forcing Hg through a jet under pressure, and their effective surface is calc. by counting and measuring microscopically a sample which is allowed to fall on a greased surface. The accurate concn. determinations necessary are carried out photometrically for coloured solutions. The quantity of liquid carried with the drops and the size of drops do not greatly affect the occupation nos. Abs. occupation nos. (no. of mols. adsorbed per sq. m.) for naphthol-yellow in H₂O decrease from 70.1×10^{16} at -45° to 45.3×10^{16} at 83° . The former figure corresponds closely to a complete unimol. layer. From the variation in adsorption with temp., the heat of adsorption is calc. to be 4200 g.-cal. per mol. at $24-50^\circ$. R. H. F.

F.p. of adsorbed liquids. R. W. Batchelor and A. G. Foster (*Trans. Faraday Soc.*, 1944, 40, 300—305).—V.p. curves for liquid and solid dioxan, and for dioxan adsorbed on porous Fe₂O₃ gel (pore radius ~ 100 Å.), were determined between -10° and 20° , in which range the plots of $\log p$ against $1/T$ are linear. In the gel system the liquid and solid v.p. lines intersect at a temp. $5.6 \pm 0.4^\circ$ below the normal f.p. In a gel with a calc. pore radius 88 Å. the depression of f.p. is $7.3 \pm 0.4^\circ$. A theoretical expression for the depression, based on the Clapeyron and Kelvin equations, is given. H₂O adsorbed on SiO₂ gel of pore radius ~ 11 Å. remains liquid in cooling to -65° . The results described refer to adsorption on porous solids in which the occurrence of capillary condensation is presumed. F. L. U.

Cluster formation and phase transitions in the adsorbed state. H. M. Cassel (*J. Physical Chem.*, 1944, 48, 195—202).—Extensions of the Langmuir adsorption mechanism to the case of multilayers cannot account for the ultimate liquefaction of the adsorbate. A relation between the crit. temp. of two- and three-dimensional condensation has been derived which accounts, in a qual. way, for the fact that higher densities can be reached in monolayers without achieving condensation than is possible in vol. phases. Discussion of discontinuities in transitions from adsorbed gas to liquid vol. leads to the view that the hysteresis observed in adsorption and desorption of vapours on porous and powdered solids represents a supersaturation phenomenon. C. R. H.

Heat of adsorption of long-chain compounds and their effect on boundary lubrication. J. J. Frewing (*Proc. Roy. Soc.*, 1944, A, 182, 270—285).—The behaviour of mild steel surfaces lubricated with solutions in white oil of long-chain halides, acids, α -substituted acids, esters, C₁₈H₃₇CN, C₁₈H₃₇CNS, and C₁₈H₃₇NO₂ was studied under high loads at low speeds. A transition from smooth sliding to "stick-slip" occurs at a temp. characteristic of the solution; the transition temp. increases with concn. It is assumed that the transition takes place when the surface concn. of the adsorbed film reaches a crit. val. which for a particular substance is independent of the temp., and a relation between the heat of adsorption U and the transition temp. is obtained and confirmed by experiment. The vals. of U show that these long-chain polar compounds are adsorbed by the interaction of their dipoles with atoms of the metal surface and not by chemical reaction. The results suggest that esters are similarly oriented at metal and aq. surfaces. G. D. P.

Contact angles and adsorption on solid surfaces. H. K. Livingston (*J. Physical Chem.*, 1944, 48, 120—124).—The known data for adsorption at solid-liquid-vapour interfaces are tabulated and show that the contact angle is generally zero, and that the solid surface is completely covered by mols. adsorbed from the vapour at saturation pressure. Doss and Rao's equation is thus verified except in cases of incomplete covering of surface and contact angle > 0 , for which no data exist. A derivation of the Doss-Rao equation for the special case of a solid surface completely covered by adsorbed mols. is given. J. O'M-B.

Capacity of a mercury electrode in presence of multivalent cations. M. Vorsina and A. Frumkin (*Acta Physicochim. U.R.S.S.*, 1943, 18, 242—263).—The influence of Ba⁺⁺, La⁺⁺⁺, and Th⁺⁺⁺⁺ on the capacity (C) of the Hg electrode at various potentials and concns. has been examined, 0.01N- and 0.001N-HCl being used as initial solutions. On addition of these cations C_{min} increases and, in the case of La⁺⁺⁺ and Th⁺⁺⁺⁺, is shifted towards less negative potentials. On the cathodic branch of the C -potential curve small additions of cations cause an abrupt rise in C leading to a max. after which C falls to a val. $>$ that in the original HCl. C_{max} in presence of La⁺⁺⁺ is approx. the same for both HCl concns., suggesting that it is La⁺⁺⁺ and not La(OH)₃ which is adsorbed. Calculations of the magnitude of the surface charge, the potential at the distance of one ionic radius from the interface, and the equiv. C of the electrode show that these cations bring about a reversal of the negative charge of the electrode surface. The data are discussed with reference to the Stern double layer theory. C. R. H.

Measurement of boundary tension by the pendent-drop method. II. Hydrocarbons. G. W. Smith (*J. Physical Chem.*, 1944, 48, 172).—Using an improved apparatus giving greater magnification, the surface tension (γ) at 20.0° of 15 hydrocarbons has been

determined. γ increases with increasing mol. wt. of straight-chain compounds and decreases with increase in the degree of branching. For cyclic hydrocarbons γ decreases with increasing saturation and is generally $>$ for the corresponding straight-chain compounds. C. R. H.

Separation of oil from the surface of water. G. Antonoff (*J. Physical Chem.*, 1944, 48, 173—174).—The possibility is discussed of collecting oil from the surface of H₂O by increasing the surface tension of the oil so that it tends to float as a lens. H₂O, on which was a layer of oil, was stirred with a stirrer with blades bent so as to give a slight inward pull. At low rotational speeds the oil collected around the axis in the form of a spherical planetary body, when it could easily be removed by means of a pipette. C. R. H.

Variation of oil-water distribution ratio of divinyl ether with concentration. W. L. Ruigh and A. E. Erickson (*Anesthesiology*, 1941, 2, 546—551).—The solubility of divinyl ether in H₂O at 37° is 5.25 g. per l. The olive oil/H₂O distribution ratio (by wt.) of the ether at infinite dilution and 37° approaches 45.3. Above a concn. of 10 wt.-% ether in the oil phase the distribution ratio is a linear function of concn. and its val. at 100% is 190.5. A method is described for measuring the oil/H₂O distribution ratio of divinyl ether (b.p. 28.3°) at 37° . G. P.

Effect of phenolic and nitrogenous substances on surface activity by complex formation. H. Bergstermann and O. Elbracht (*Biochem. Z.*, 1941, 310, 64—82).—Data for the surface tension (γ) of aq. solutions of various phenols and their derivatives and of N bases, and also for their mixtures, are graphically represented. The introduction of hydrophobic groups and the marked hydrophobic properties of the reaction products (cf. Labes et al., A., 1938, I, 518; 1939, II, 528) are reflected in their γ -depressing effect, which is the additive effect of the single components and is apparent at concns. $<$ those necessary for any pptn. reaction. F. O. H.

Harkins' "final spreading coefficient" and Antonoff's "rule." W. Fox (*J. Physical Chem.*, 1944, 48, 158—159).—The author's experiments (A., 1943, I, 13) show that Antonoff's "rule," though not general, is applicable to a no. of liquid-liquid-gas systems. From this and Harkins' expression of Antonoff's "rule" in terms of the "final spreading coeffs.," Antonoff's theory is concluded to be invalid. J. O'M-B.

Foam formation in organic liquids. E. G. King (*J. Physical Chem.*, 1944, 48, 141—154).—Foam formation for 47 surface-active agents such as Emulphor O (I), Ninols, Aerosol Ay, and Nacconol NR in various org. solvents of commercial purity has been examined. Foaming capacity and stability were measured by time of expiration of the foam and where possible by its vol. Foaming seems in general $<$ in aq. solution though some org. foams are comparable in vol. and stability with aq. foams. The foaming capacity of (I) is greatest in hydroxylic solvents. Foaming properties usually increase with the surface tension γ of the solvent, but in some solvents of high γ such as PhNO₂, furfuraldehyde, and dioxan (I) shows no tendency to foam and does not depress their γ . The lowering of γ which often occurs with foam formation is not general. η and v.p. are not prime factors in foam initiation, but a high η tends to stabilise any foam that is formed. High η also inhibits aeration and decreases the rate at which equilibrium is set up at the interface. The surface activity and propensity for foam formation of colloidal electrolytes depend on structural connexions between solvent and solute, but these are complex. Thus (I) is efficacious in glycol but not in glycerol, whilst for Ninol 555 base the converse obtains. J. O'M-B.

Minimum and equilibrium concentrations. A. M. Belousov and A. P. Terenteeva (*J. Appl. Chem. Russ.*, 1940, 13, 463—469).—The product $[Ba^{++}] \times [SO_4^{--}]$ at which turbidity produced by BaSO₄ becomes visible (Tyndall effect) is 100—1000 times the solubility product; when the turbidity is observed with the unaided eye, the ratio is 10^3-10^4 . It is higher when $[SO_4^{--}]$ is lower. J. J. B.

Rate of sedimentation of non-flocculated suspensions of uniform spheres.—See B., 1944, I, 321.

Effect of electric field on Tyndall scattering. R. S. Subrahmanya, K. S. G. Doss, and B. S. Rao (*Proc. Indian Acad. Sci.*, 1944, 19, A, 405—413).—The effect of an electric field on sols of AgI, stearic acid (I), and benzopurpurin 6B (II) has been investigated. The equiv. spherical diameters in the AgI and (I) sols were 104.8 and 390.8 m μ . By combination of the schlieren and Langmuir methods the shapes of the particles were found to be: AgI not appreciably anisometric; (I) disc-shaped; (II) rod-shaped. The electric field (~ 100 v. d.c. or 220 v. a.c.) was applied by Pt or C sheet electrodes, the sol being illuminated so that the light was incident on the sol horizontally and the scattered light was viewed transversely in the horizontal and vertical directions. The field could be applied longitudinally parallel to the beam, or transversely in the vertical or horizontal directions. Both d.c. and a.c. gave identical results with (I) and (II). AgI showed no effect. For large disc- or rod-shaped particles oriented by a linear field there is enhanced scattering when the field is put on, if the plane of incidence and observation is perpendicular to the field, but diminished scattering for other orientations. W. R. A.

Colloidal system carbon dispersed in xylene. V. R. Damerell and A. Urbanic (*J. Physical Chem.*, 1944, **48**, 125—133).—Lecithin, Cu oleate, Co naphthenate, and Na dioctyl sulphosuccinate increase the degree of dispersion of C in xylene in the order given, the effect being increased by drying. Cataphoresis of the organosols is unaffected by the degree of dryness; the particles are all negatively charged. Dispersion increases with adsorption for Cu oleate and Co naphthenate. Pptn. is brought about by addition of EtOH or H₂O, by heat, and by an electric field. Low temp. to -5° has no effect. H₂O hinders the adsorption of the surface-active material and hence decreases the stability. The source of the charge in such systems may be due to dissociation of the polar-non-polar additive in the presence of a trace of H₂O, or to slight dissociation in the pure xylene. J. O'M-B.

Effect of surface-active agents on dispersions of calcium carbonate in xylene. V. R. Damerell and R. Mattson (*J. Physical Chem.*, 1944, **48**, 134—141).—Zn, Ba, and Na dioctyl sulphosuccinates (I), lecithin (II), and Mg oleate cause dispersion of CaCO₃ in xylene. Drying causes decrease in the amount of coarse material, but the amount of colloidal material falls by 4%. Dispersion is independent of the concn. of (I) down to a low concn. The dispersing agent is positively adsorbed and for (I) forms a unimol. layer. The organosols are milky-white and opalescent, coagulated by H₂O, 95% Et₂O, and by heat. Cooling to 0° has no effect. The particles are positively charged except with (II), when they are both positive and negative. The origin of the charge in dry solution is difficult to explain. J. O'M-B.

Aqueous solutions of sodium mercurochrome and substances incompatible with them. P. Duquenois (*Rev. Fac. Sci. Istanbul*, 1943, **8**, A, 153—157).—Aq. solutions of Na mercurochrome (Na₂ 2:7-dibromo-4-hydroxymercurifluorescein) (I) are stable sols which are coagulated by inorg. and org. acids and by salts of Li, NH₄, heavy metals, and alkaloids. The solutions sometimes become decolorised and lose their fluorescence. Natural colloids readily adsorb (I) from solution. C. R. H.

Laminar-dispersed substances. I. Colloidal nickel hydroxide. A. Berger (*Kolloid-Z.*, 1943, **103**, 185—202).—Ni(OH)₂ sols with laminar particles are easily prepared and are stable, and have been examined largely by the methods used for chain mols. X-Ray data give information on the size and shape of the primary particles. The axial ratio can be deduced from η measurements, provided that the necessary conditions apply. Using this axial ratio, measurements of streaming birefringence enable the vol. and hence the dimensions of the particles to be calc. Measurements of light scattering and examination with the ultra-microscope are also carried out. The prep. of Ni(OH)₂ sols by peptisation of pptd. Ni(OH)₂ with H₂O is described, and the course of peptisation followed by determining the concn. of the sol. Peptisation curves are S-shaped, indicating an induction period. X-Ray investigation reveals an aggregation effect, which is diminished by addition of glucose. The change in particle dimensions during peptisation is examined. The "mol. wt." of the primary particles is estimated to be 1.1×10^6 . Secondary particles are examined by the methods of the ultra-microscope and sedimentation velocity. R. H. F.

Solvent properties of detergent solutions.—See B., 1944, II, 287.

Electrical anisotropy of xerogels of hydrophilic colloids. I. S. E. Sheppard and P. T. Newsome (*J. Chem. Physics*, 1944, **12**, 244—248).—The degree of orientation in an alternating electric field of discs of colloid materials, e.g., proteins, plastics, in which a fibrous structure was produced by stretching to <100%, has been measured. Induced electrical anisotropy is shown only by xerogels that are hydrophilic, and its relation to field strength, thickness, R.H., and H₂O content is discussed. Whilst most show dependence on R.H. and absorbed H₂O content, the effect with polyvinyl alcohol does not depend on the absorbed H₂O. W. R. A.

Form and size of dissolved particles from diffusely scattered X-rays at very small angles. O. Kratky and A. Sekora (*Naturwiss.*, 1943, **31**, 46—47).—When X-rays are passed into an assemblage of small particles, two types of scattering result, one at large angles, due to mol. arrangement, and the other at very small angles, due to the shape and form of the particles. A knowledge of the structure of the particle is unnecessary in dealing with the small-angle scattering. If a large no. of these particles are irregularly placed at distances large compared with the size of the particles, the total scattering effect can be obtained by adding the intensities due to single particles, as in the case of a gas. The introduction of a liquid as a medium does not affect the result. It is possible to use this method to investigate the form and size of colloidal particles. Chymotrypsin, a protein with an approx. spherical mol., and of mol. wt. 1 Svedberg unit, is taken as an example. The curve of intensity against scattering angle is obtained experimentally, and compared with that obtained by assuming Fraunhofer scattering at spherical particles of radius 23 Å. The theoretical and experimental curves agree closely. It is possible to obtain the approx. axis ratios of non-spherical particles. A. J. M.

Consistency of plastic suspensions of the Bingham type. H. de Bruijn, H. Dols, and C. Kuyper (*Rec. trav. chim.*, 1943, **62**, 696—704).—The velocity of deformation (D)—shearing stress (τ) and the fluidity (ϕ)— τ diagrams are given for C black in light mineral oil at 20° and 40°, and agree with the authors' theoretical predictions. The plasticity of such a system is almost entirely a function of the temp. coeff. of the ϕ of the intermicellar liquid. For measurements at high τ , turbulence vitiates the results; a corrective method, derived from the known temp. coeff. of the plasticity, is indicated. To describe the curved part of the D - τ diagram more exactly by consts., the concept of liquidation tendency, i.e., the slope of the straight section of the relation, is introduced; it is best obtained from the D/τ - τ relation. J. O'M-B.

Mol. wt. of high-molecular substances by the method of longitudinal scattering of infra-red rays. W. W. Lepeschkin (*Kolloid-Z.*, 1943, **105**, 141—144).—The author's earlier apparatus for the measurement of the scattering of infra-red rays (Plotnikow effect) is improved to enable substances of lower mol. wt. to be studied. The method is used to determine the mol. wt. of the haemocyanin of *Helix pomatia*, using ovalbumin as reference substance. The vals. obtained agree with those obtained by other methods. J. F. H.

High-molecular polymerisation of low-molecular substances by the method of longitudinal scattering of infra-red rays. W. W. Lepeschkin (*Kolloid-Z.*, 1943, **105**, 144—147; cf. preceding abstract).—The dependence of the Plotnikow effect on the mol. wt. of the scattering substance is used to study the polymerisation of aq. solutions of CH₂O, (I), ψ -isocyanine (II), resorcinol (III), quinol (IV), and a mixture of H₂O and C₂H₅N in the mol. ratio 3:1. All show strong polymerisation except (IV), which is more strongly polymerised in EtOH and Et₂O solutions. Dilution of (I) reverses the polymerisation. The polymerisation of (II) and (III) is reversed by warming. EtOH solutions of (II) are unimol. J. F. H.

Relations between tension, stretching birefringence, and deformation mechanism for rubber-like materials. J. J. Hermans (*Kolloid-Z.*, 1943, **103**, 210—221).—The curled-mol. theory of elasticity of rubber-like substances is discussed in relation to cross-linking between mol. chains, and a theory of deformation is developed on a purely physical basis. The distance between the ends of a mol. is determined by a diffusion equilibrium, which is displaced when an external force is applied. The increase in entropy, the extension, and the optical anisotropy on stretching are calc. for the case where no change of vol. occurs on stretching. Birefringence is derived by calculating the polarisabilities in two directions and expressing their difference in terms of n . This difference is \propto the applied tension. The relaxation time is the smaller the greater is the degree of netting of chains. The limits of validity of the theory are discussed. R. H. F.

Chemical constitution and colloid structure of fibre-forming synthetic polymers. I. Chemical constitution, intermolecular bonding, and colloid structure. W. Broser, K. Goldstein, and H. E. Krüger (*Kolloid-Z.*, 1943, **105**, 131—141).—Theoretical. These substances can be divided into two classes: (a) the polymeric hydrocarbons and their derivatives and (b) the "mesomeric chain polymers" in which the mesomeric groups (CO·NH₂, ester, urea groups, etc.) form part of the chain. The name "meta-zwitterion" is suggested for the prevailing state of the mesomeric groups, intermediate between the non-polar and zwitterion forms. In group (a) undirected dispersion forces are operative and a "cotton-plug" structure without any marked autonomous arrangement is formed. In group (b) dipole forces are operative and a micellar structure results. The bonding between these meta-zwitterions is intermediate between heteropolar principal valencies and normal dipole forces, for which the term "meta-ionic relation" is suggested. The common colloidal structure and hence similarity in physical properties of type (b) polymers are due to the presence of a common meta-ionic bonding and thus ultimately to similar chemical constitution. The meta-ionic bond should be considered the intermol. link between H and N in type (b) polymers rather than the H bond, if necessary with reference to a possible mesomerism: meta-ionic bond \longleftrightarrow H bond. J. F. H.

Combination of fibrous proteins with acids. G. A. Gilbert and E. K. Rideal (*Proc. Roy. Soc.*, 1944, **A**, 182, 335—346).—An approx. titration equation is developed for the reaction between fibrous proteins and acids, in which account is taken of the valency and intrinsic affinities of the acid anions, and of the limited no. of adsorption sites available for anions. The transition from sol. to fibrous proteins is traced in order to demonstrate that the main difference between the titration curves of the two types of protein arises from the difference of potential developed during the adsorption of protons. G. D. P.

Opacity changes during the coagulation of sols by electrolytes. M. Prasad, S. Guruswamy, and N. A. Padwal (*Proc. Indian Acad. Sci.*, 1944, **19**, A, 389—400).—Changes in opacity during the coagulation of Th(OH)₄, Sn(OH)₄, and Zr(OH)₄ sols have been investigated with the apparatus previously described (cf. A., 1943, I, 256). The results enable comparison of the coagulating power of electrolytes

to be made and show that Smoluchowski's equation is applicable only for rapid coagulation. Increased temp. and addition of MeOH or EtOH accelerate coagulation. W. R. A.

VI.—KINETIC THEORY. THERMODYNAMICS.

Thermodynamics of dissociation of acids. G. Briegleb (*Naturwiss.*, 1943, 31, 62—65).—Fundamental equations are given for the expression of acid strength in terms of intramol. polarisation and associated energy relations. L. J. J.

Effect of temperature on the electrolytic dissociation in strong electrolytes. I. Nitric acid. N. R. Rao (*Indian J. Physics*, 1943, 17, 295—299; cf. A., 1943, I, 153).—The degree of dissociation (α) of HNO_3 at various temp. has been calc. by comparing the intensity of the Raman ν at 1050 with that at 1300 cm^{-1} . With rise in temp. α decreases. W. R. A.

Influence of common ion on the dissociation of some strong electrolytes. I. Sulphuric acid and bisulphates. N. R. Rao (*Indian J. Physics*, 1943, 17, 283—286).—By Raman spectral methods the influence of added H^+ (from HCl and HClO_4) and SO_4^{2-} (from sulphates) ions on the dissociation of H_2SO_4 has been studied. Dissociation is decreased by H^+ ions. Dissociation of HSO_4^- is decreased by H^+ and enhanced by SO_4^{2-} ions. W. R. A.

Parachor of potassium dichromate and constitution of chromic acid.—See A., 1944, I, 214.

Relative free energies and dissociation constants of microscopic ions. T. L. Hill (*J. Physical Chem.*, 1944, 48, 101—111).—Microscopic dissociation constns. and relative standard free energies of ions may be calc. from experimental dissociation constns. for a no. of compounds. The average effects of charges in different positions in the mols. on their microscopic dissociation constns. are estimated. Thus approx. vals. of the microscopic constns. can be obtained for those substances for which there are no experimental data. The charge effects are generally represented by the equation $\text{p}K = 2.00 d$, where d is the interchange distance, and in general $\Delta \text{p}K_a - \text{p}K_a^0 = c/d$, where $\text{p}K_a^0$ is the $\text{p}K$ val. in the absence of charge effects, and c is a const. For dicarboxylic acids the relative free energy of dissociation is the lower, the closer the second CO_2H is to the dissociating CO_2H . $\text{CH}_3(\text{CO}_2\text{H})_2$ and $\text{H}_2\text{C}_2\text{O}_4$ are anomalous owing to H bond formation between the dissociated and undissociated CO_2H . There is no evidence for H bonds in the amines examined. Analogies between the relative free energies and spectroscopic energy levels, and between the microscopic dissociation constns. and spectral lines, are indicated. J. O'M-B.

Dissociation constant and isoelectric point of sulphanilamide. A. J. Llacer (*Anal. Assoc. Quím. Argentina*, 1943, 31, 139—146).—Acidic and basic vals. of k for $p\text{-NH}_2\text{-C}_6\text{H}_4\text{SO}_2\text{NH}_2$ are respectively 3.55×10^{-11} and 7.01×10^{-12} at 25° , 6.37×10^{-11} and 1.20×10^{-11} at 30° , and 7.41×10^{-11} and 2.04×10^{-11} at 37° . There is an isoelectric zone between pH 4 and 9. F. R. G.

Application of the method of continuous variations to complex ion formation in cupric salts containing chloride ions. T. Moeller (*J. Physical Chem.*, 1944, 48, 111—119).—Alterations in the absorption spectra of cupric salts in solution on the addition of alkali halides indicate the formation of a complex ion containing Cl. Application of the above method (cf. Job, A., 1928, 589) shows that CuCl_4^{2-} (I) is formed but gives no information on the presence of other complexes. (I) is unstable except at high concns. of Cu^{2+} and Cl^- . Colour changes are explained by a shift in the equilibrium between $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ and CuCl_4^{2-} , the latter being produced by an auto-complexing process. It is probably yellow, but the continued presence of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ prevents attainment of this colour by the solution. J. O'M-B.

Activities of components in anstenite. J. Gerasimov (*Acta Physicochim. U.R.S.S.*, 1943, 18, 275—299).—A method of calculating the activities of the components of a binary solution from heterogeneous equilibrium constns. has been devised. For calculation purposes austenite (I) can be regarded either as a solid solution of C in $\gamma\text{-Fe}$ or as a solid solution of Fe_3C in $\gamma\text{-Fe}$, and component activities at 800—1100° have been calc. on both assumptions, although the second assumption is more convenient. The integral heats of dissolution of Fe_3C and the solubilities of $\alpha\text{-ferrite}$ and cementite (II) in (I) have been calc. Equations for the free energy of formation of (II) and of a less stable "regular" Fe_3C modification in Fe are given. C. R. H.

Gas-gas equilibrium and phase equilibria in binary systems. I. Kritschewski and D. Ziclis (*Acta Physicochim. U.R.S.S.*, 1943, 18, 264—274).—Equilibrium data for $\text{NH}_3\text{-N}_2$ and $\text{NH}_3\text{-CH}_4$ obtained over the range 90—148° and 45—100° respectively and at pressures $>10,000$ kg. per sq. cm. and for $\text{NH}_3\text{-N}_2\text{-H}_2$ (two different compositions) over the range 100—105° and at pressures >5500 kg. per sq. cm. prove the existence of limited mutual solubility of NH_3 and N_2 at temp. $>$ the crit. temp. of NH_3 . C. R. H.

System beryllium oxide-water. H. Terem (*Rev. Fac. Sci. Istanbul*, 1943, 8, A, 99—111).—Only one hydrate of BeO exists, viz., $\text{BeO}\cdot\text{H}_2\text{O}$, which is stable at temp. $<220^\circ$. Between 240° and 260° loss of H_2O is rapid and only traces of H_2O remain at 280° . BeO prepared by calcining at 300—400° is hygroscopic but if calcined at higher temp. its hygroscopicity is much lower. The uptake of H_2O is regarded as an adsorption process, the efficiency of which depends on the temp. of calcination. C. R. H.

Interpretation of distribution equilibria between molten metals and molten salts. E. Heymann, R. J. L. Martin, and M. F. R. Mulcahy (*J. Physical Chem.*, 1944, 48, 159—160).—A reply to criticism of the authors' paper (A., 1944, I, 63) by N. W. Taylor. J. O'M-B.

Complex formation in the system lead chloride-sodium chloride-water. B. V. Gromov (*J. Appl. Chem. Russ.*, 1940, 13, 337—344).—The solid phase in saturated solutions of PbCl_2 and NaCl in H_2O consists either of PbCl_2 , or of NaCl, or of both. There is no compound of PbCl_2 with NaCl, and the rise of solubility of PbCl_2 caused by NaCl must be due to interionic forces. J. J. B.

Equilibrium in the system lead sulphate-sodium chloride-water. B. V. Gromov (*J. Appl. Chem. Russ.*, 1940, 13, 345—356).—Solutions saturated with NaCl, PbCl_2 , and PbSO_4 at 25° , 50° , and 100° contain NaCl 23.4, 25.0, 26.0%, PbCl_2 2.34, 4.60, 12.7%, and Na_2SO_4 3.40, 2.05, 1.08%, respectively. Solutions saturated with NaCl, Na_2SO_4 , and PbSO_4 at the same temp. contain NaCl 22.3, 24.2, 26.3%, PbCl_2 0.60, 0.62, 1.43%, and Na_2SO_4 7.1, 5.37, 4.76%, respectively. Diagrams of state are given. J. J. B.

System magnesium selenate-selenic acid-water at 30° . H. Furukawa and G. B. King (*J. Physical Chem.*, 1944, 48, 174—178).—Solubility data for the system are recorded in tabular and triangular diagrammatic form. Four stable solid phases exist in equilibrium with H_2SeO_4 , viz., $\text{MgSeO}_4\cdot 6\text{H}_2\text{O}$, $\text{MgSeO}_4\cdot 4\text{H}_2\text{O}$, $\text{MgSeO}_4\cdot \text{H}_2\text{SeO}_4\cdot 6\text{H}_2\text{O}$, and, probably, MgSeO_4 at 0—35.50, 35.50—43.08, 43.08—56.79, and 56.79—77.69% of H_2SeO_4 respectively. C. R. H.

Polytherm of the ternary system $\text{NaNO}_3\text{-Na}_2\text{CrO}_4\text{-H}_2\text{O}$. M. I. Ravitsch (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 233—236).—Solution isotherms for the ternary system were determined at 0° , 25° , 50° , and 98.5° . Within this temp. range no evidence could be found for the formation of a double salt. Systems containing $\text{Na}_2\text{CrO}_4\cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{CrO}_4\cdot 4\text{H}_2\text{O}$ were also investigated. The results are presented in tables and graphs. V. B.

System $\text{NaAlSiO}_3\text{-CaSiO}_3\text{-Na}_2\text{SiO}_3$. J. Spivak (*J. Geol.*, 1944, 52, 24—52).—Thermal equilibrium relationships in this system have been investigated by the quenching method. Thermal data for the system nepheline-wollastonite-Na metasilicate are tabulated, and the results are presented in the form of equilibrium diagrams. Their bearing on related systems of the $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$ tetrahedron, and their petrological significance, are discussed. L. S. T.

Heat of formation of olenm. F. D. Miles, H. Niblock, and D. Smith (*Trans. Faraday Soc.*, 1944, 40, 281—295).—Differential heats of addition of liquid SO_3 to oleum containing up to 70% of free SO_3 have been determined (1) directly and (2) by measuring the heat of vaporisation of SO_3 from oleum. Vals. given by method (1) are generally $<$ those given by method (2), probably owing to varying heat content of liquid SO_3 . Higher vals. are given by the direct method when the SO_3 has been redistilled once or twice with P_2O_5 . The heat of combination of liquid SO_3 with H_2O has been redetermined by adding SO_3 to aq. H_2SO_4 and using Brønsted's data for the change in heat content of the acid. The result is 20.00 kg.-cal. per mol. at 30° . Integral heats of mixing liquid SO_3 with H_2O at 30° to form 1 g. of acid are given for the range 0.400—0.950 g. SO_3 . F. L. U.

Free energies of solutions of single and multiple molecules. W. J. C. Orr (*Trans. Faraday Soc.*, 1944, 40, 320—332).—Expressions for free energies, heats and entropies of mixing of single and multiple mols. are obtained on the basis of the statistical model of a strictly regular solution as defined by Fowler and Guggenheim. The limits of validity of the formulæ are discussed, and the theoretical calculations are compared with available thermodynamic data for the rubber- C_6H_6 system. F. L. U.

VII.—ELECTROCHEMISTRY.

Effect of temperature on the potential of glass electrode systems for pH measurement. N. Koyenuma (*Naturwiss.*, 1943, 31, 44—46).—A general expression for the temp. coeff. of a glass electrode is deduced. Differentiation of the equation $E_1 - E_2 = RT(\text{pH}_2 - \text{pH}_1)/F$, and substitution of the vals. $\text{pH}_2 = 4.62$ and $dE_2/dT = 0.085$ for a standard acetate buffer gives the temp. coeff. $dE_1/dT = 0.833 - 0.1985\text{pH}_2 - 59\text{dpH}_2/dT$. A similar equation can be obtained and extended on the basis of thermodynamics. The result in this case is $dE/dT = \text{const.} - 0.1985\text{pH} - 59\text{dpH}/dT$ —

$1/F[dU/dT(\log T/T_0)]$. The evaluation of the const. and the last term of the above expression is carried out for 0.1N-HCl.

A. J. M.

Reduction of nitroguanidine. XII. Oxidation potentials of the nitroguanidine-nitrosoguanidine and nitrosoguanidine-aminoguanidine systems. C. Hahn, E. Pribyl, E. Lieber, B. P. Caldwell, and G. B. L. Smith (*J. Amer. Chem. Soc.*, 1944, 66, 1223—1226; cf. A., 1938, II, 7).—Measurement of oxidation-reduction potentials shows that the system, nitroguanidine \rightleftharpoons nitrosoguanidine (I) has E_0 0.88 v. at pH 2—7 [reaction being $[C(NH_2)_2 \cdot NH \cdot NO_2]^+ + 2H^+ + 2e \rightarrow [C(NH_2)_2 \cdot NH \cdot NO]^+ + H_2O$], but 0.85 v. at pH 8—1 [reaction being $[NH_2 \cdot C(NH_2) \cdot N \cdot NO_2]^- + 2H^+ + 2e \rightarrow [NH_2 \cdot C(NH_2) \cdot N \cdot NO]^- (A) + H_2O$]; at pH 7—8 E_0 is indefinite. The system (I) \rightleftharpoons aminoguanidine has E_0 0.66 v. at pH 1—5 [reaction being $[C(NH_2)_2 \cdot NO]^+ + 4H^+ + 4e \rightarrow [C(NH_2)_2 \cdot NH \cdot NH_2]^+ (B) + H_2O$], indefinite at pH 6—8, 1.03 v. at pH 8—10 [reaction being $(A) + 6H^+ + 4e \rightarrow (B) + H_2O$], and 0.97 v. at pH 10—12 [reaction being $[NH_2 \cdot C(NH) \cdot N \cdot NO]^- + 6H^+ + 4e \rightarrow NH_2 \cdot C(NH) \cdot NH \cdot NH_2 + H_2O$]. Vals. of $-\Delta F$ for the five named transformations are 40.6, 39.2, 61, 143, and 134, respectively, and of $\log K$ are 29.8, 28.8, 45, 70, and 65, respectively.

R. S. C.

Effect of the background electrolyte on polarographic waves of cadmium and lead. S. P. Schaikind (*J. Appl. Chem. Russ.*, 1940, 13, 455—462).—The height of the polarographic waves of Cd²⁺ in KCl, Na₂SO₄, ZnCl₂, and ZnSO₄ solutions, and of Pb²⁺ in KCl and ZnCl₂ solutions, is $\propto [Cd^{2+}]$ or $[Pb^{2+}]$. The coeff. of proportionality is independent of the concn. of KCl but is the greater the higher is the dilution of Na₂SO₄ (0.1—0.9M.), ZnCl₂ (0.1—1.8M.), or ZnSO₄ (0.1—1.8M.).

J. J. B.

Behaviour of γ -keto- and aldehydo-acid derivatives at the dropping mercury electrode.—See A., 1944, II, 298, 307.

Reduction potentials of acridines, with reference to their antiseptic activity. B. Breyer, G. S. Buchanan, and H. Duewell (*J.C.S.*, 1944, 360—363).—The reduction potentials ($E_{1/2}$) of acridine, amino-acridines, and other derivatives have been obtained by means of the dropping Hg cathode. The reduction takes place in two steps of equal height, only one H atom being taken up with each step, meaning that the first reduction product is a free radical. The first reduction takes place at the N atom and the second at the C₁₅ atom. There is a definite relation between $E_{1/2}$ and chemotherapeutic activity, in the sense that acridines with for the first-stage reduction more negative than -0.400 v. at pH 7.3 are biologically the most active.

C. R. A.

VIII.—REACTIONS.

Experimental determination of the decrease of pressure in the blue cone of flames. V. Vasilescu (*Ann. Physique*, 1943, [xi], 18, 190—208).—Measurements are reported with H₂—O₂—N₂ mixtures of known composition in order to verify Riemann's formula connecting the velocity of an impulse wave in a gaseous medium with the variation of pressure and density of the medium. Combustion in the stationary blue cone represents, on Jouguet's theory, impulse waves with decrease of pressure. This pressure decrease Δp was measured by two methods and results are compared with vals. calc. by Riemann's formula. Data show that Δp (calc.) is $> \Delta p$ (experimental), and this arises from the fact that the former corresponds with the interior zone of the cone, and the latter with the region around the base of the cone. It is assumed that there is a gain of pressure in the flame following its emergence from the cone, and the sum of this gain and Δp (experimental) should equal Δp (calc.). This gain is calc. and satisfactory agreement is found provided the blue cone is not very pointed. For more pointed cones Δp (calc.) $< \Delta p$ (experimental) corr. for pressure gain.

N. M. B.

Chemiluminescence of flame. V. Kondratev (*Uspechi Chim.*, 1943, 12, 308—317).—The radiation of all flames in diluted gases and of some flames under atm. pressure is a chemiluminescence, i.e., its intensity is $>$ that of the thermal radiation, the dispersion of its intensity is not accounted for by probability, and it is quenched by foreign mols. The luminescence occurs either after recombination of free atoms or radicals or in an exchange reaction. The concn. of luminescent atoms or mols. sometimes is \propto rate of reaction; if the coeff. of proportionality is not affected by an external factor, this factor does not affect the mechanism of the reaction.

J. J. B.

Explosive reactions. II. Propagation of gaseous explosions. M. F. R. Mulcahy and A. Yoffe (*J. Proc. Austral. Chem. Inst.*, 1944, 11, 134—146).—A review of published work on flame propagation through gases.

L. J. J.

Kinetics of the reaction between chlorine and nitric oxide. E. M. Stoddart (*J.C.S.*, 1944, 388—393).—The fall in velocity coeff. for the reaction between Cl₂ and NO is due to ageing of the walls of the reaction vessel owing to adsorption of NOCl. Adsorbed NOCl cannot be completely removed by evacuation and only with great difficulty by heat. The retarding effect of NOCl is reduced by

drying the reactants, suggesting that this effect is due to adsorption of NOCl on the H₂O content of the glass surface. When this effect is absent the reaction is termol.

C. R. H.

Explosions with degenerate branching. K. G. Fahlbusch and W. Jost (*Naturwiss.*, 1943, 31, 148).—In the oxidation of COMeEt the induction times for the slow reaction and explosion pass steadily into each other. If τ is the induction time, the plot of $\log \tau$ against $1/T$ is two straight lines, one for the slow reaction, the other for the explosion. The slope of the two lines is almost the same.

A. J. M.

Spontaneous character, and indifference to the catalytic effect of oxygen, of the polymerisation of acetaldehyde at very low temperatures. M. Letort and X. Duval (*Compt. rend.*, 1943, 216, 608—610).—When MeCHO is kept at the m.p. (-123.5°) for 2 hr. it polymerises. The polymerisation is unaffected by the purity of the MeCHO, and by the vessel in which the reaction occurs. It occurs with the substance from which traces of air have been removed and in absence of air. Probably it is not catalysed.

A. J. M.

Theory of chain copolymerisation reactions. R. Simha and H. Branson (*J. Chem. Physics*, 1944, 12, 253—267).—Mathematical. The kinetics of chain polymerisations is developed for reactions consisting of the three steps: (a) activation of a stable monomer, (b) growth of activated polymer radical by addition of monomer, (c) stabilisation of growing chains by (i) monomer addition, (ii) growing polymer. The general over-all reaction, determination of radical distribution, special rate equations, copolymer composition, and size distribution are discussed.

W. R. A.

Kinetics of the reaction between silver perchlorate and methyl iodide. M. F. Redies and T. Iredale (*J. Physical Chem.*, 1944, 48, 224—230).—The reaction between AgClO₄ and MeI in various solvents and at various temp. has been investigated. Two forms of kinetics appear to be involved, pseudo-bimol. (second order) at low concns. and a 2.5 order at higher concns. With Et₂O as solvent a third-order rather than a 2.5-order reaction appears to be involved. The possibility of the reaction being heterogeneous because of the presence of pptd. AgI is discussed. The energies of activation are $\sim 11,000$ — $13,000$ g.-cal.

C. R. H.

Mechanism of some ionic reactions in aqueous solutions. J. Weiss (*J.C.S.*, 1944, 309—311).—In the reduction of FeCl₃ by Sn^{II} salts it is suggested that SnCl₂ forms the complex ion SnCl₄²⁻ which takes part in the reaction according to $Fe^{3+} + SnCl_4^{2-} \rightleftharpoons Fe^{2+} + SnCl_4^{2-}$ and $Fe^{3+} + SnCl_4^{2-} \rightarrow Fe^{2+} + SnCl_4^{2-}$, the equilibrium being $SnCl_2 + 2Cl^- \rightleftharpoons SnCl_4^{2-}$. This last equation shows that presence of HCl increases $[SnCl_4^{2-}]$ as well as increasing $[Fe^{3+}]$ by preventing hydrolysis of FeCl₃, and it is shown that under such conditions the reaction is bimol. The data for this reaction do not support Shaffer's hypothesis for oxidation-reduction processes, according to which reactions between mols. or ions, where one component is capable of a bivalent oxidation (or reduction) but the other only of a univalent reduction (or oxidation), do not take place or proceed only immeasurably slowly.

C. R. H.

Conductometric study of the velocity of the reaction $[CO(NH_2)_2 \cdot Cl]^{++} + OH^- \rightarrow [Co(NH_2)_2 \cdot OH]^{++} + Cl^-$. H. A. Puente and A. L. M. Lelong (*Anal. Asoc. Quim. Argentina*, 1943, 31, 5—22).—The reaction has $h = 78 \pm 1$ at 25°. Special precautions were adopted owing to the rapidity of the reaction.

F. R. G.

Rearrangement of alkyl halides. F. R. Mayo and A. A. Dolnick (*J. Amer. Chem. Soc.*, 1944, 66, 985—990).—The rate of equilibration of Pr ^{α} Br with Pr ^{β} Br at 250° (gives 67% of Pr ^{β} Br) is somewhat erratic owing to traces of impurities. It is increased by O₂ (air), HBr, C₂H₆, NEt₃, or NHBu₂ (gives a quaternary salt), is decreased by *o*-C₆H₄(OH)₂ (very effective), Pr ^{α} OH, or Pr ^{β} O, but is unaffected by crushed Pyrex glass, H₂O, or illumination. AlBr₃ has a great accelerating effect but at 250° causes tar formation; at 70° it leads to 85% and at 26° to 91% of Pr ^{β} Br. The rate is much faster in the liquid than in the vapour phase; this is not a dilution effect since the rate is rapid in dil. solution in PhBr. Reaction proceeds by loss and addition of HBr, two mechanisms (chain reaction and non-Markovnikov addition) proceeding simultaneously. Bu ^{α} Cl and Bu ^{γ} Cl are unaffected at 250° but at 300° are equilibrated to give 78—92% of Bu ^{γ} Cl (and tar); this reaction is unaffected by air or *o*-C₆H₄(OH)₂ but is accelerated by NEt₃Cl⁺ (CH₂Cl)₂ and CHMeCl₂ or (CH₂Br)₂ and CHMeBr₂ are not equilibrated by AlBr₃ but some halogen exchange occurs with (CH₂Cl)₂ at 100°. (CH₂Br)₂ and CHMeBr₂ are equilibrated by NEt₃Br at 250° to give 76—82% of (CH₂Br)₂. Although non-Markovnikov addition of HHal to olefines usually gives the thermodynamically more stable isomeride (cf. above), CH₂:CHBr is exceptional.

R. S. C.

Useful life [rate of hydrolysis] of pyro-, meta-, and tetra-phosphates.—See B., 1944, I, 304.

Hydrolysis of maltohexaose.—See A., 1944, II, 326.

Rate of nitration of toluene with mixed acid.—See B., 1944, II, 269.

Reaction of water-gas conversion in quartz vessels. V. Kondratyev and M. Ziskin (*Acta Physicochim. U.R.S.S.*, 1943, 18, 197—209).—The rate of reaction of CO_2 - H_2 mixtures on passing through heated SiO_2 tubes is not governed by the reaction time but by the surface area of the reaction tube, a large area having an inhibiting effect. The amount of H_2 transformed into H_2O (γ) increases with temp. according to an exponential law, but equilibrium is far from being attained at 800° . A reaction scheme based on the assumption of catalytic activity on the part of O_2 is proposed, and it follows from calculations that $\gamma_{\text{max}} \propto e^{-(E_{\text{III}} - \frac{1}{2}E_{\text{I}})/RT}$, where E_{III} and E_{I} are the respective activation energies of stages $\text{H} + \text{CO}_2 \rightarrow \text{CO} + \text{OH}$ and $\text{O}_2 + \text{H} \rightarrow 2\text{OH}$. C. R. H.

Interaction of oxygen and carbon filaments at high temperatures. R. F. Strickland-Constable (*Trans. Faraday Soc.*, 1944, 40, 333—343).—C filaments were electrically heated in O_2 at low pressures 0.02—0.5 mm.) over a temp. range of 900—2000° and the reaction was studied by pressure measurement and analysis. CO is the chief and primary product, only small amounts of CO_2 being formed. The reaction is of the first order. The rate increases from 900° to 1100°, is const. between 1600° and 2000°, and in the intermediate range is very sensitive to the immediate past history of the filament. No sorption of O as oxides in freshly outgassed filaments at 1000° was observed. The importance of avoiding activation of gas mols. by thermionic emission from the filament at high temp. is stressed and means of doing this are described. F. L. U.

Inflammability and explosibility of powders used in the plastics industry.—See B., 1944, II, 289.

Extraction of potassium carbonate from wyomingite. Kinetics of base-exchange reaction with sodium carbonate.—See B., 1944, I, 331.

Catalysis of the reaction between dichromate and aromatic amines by the oxalate ion. C. R. Viswanadham and G. G. Rao (*Current Sci.*, 1944, 13, 47—48).—Observations with 8 amines, in presence of dil. H_2SO_4 , show that 1 ml. of 0.2N- $\text{Na}_2\text{C}_2\text{O}_4$ causes the characteristic reaction colour to appear in 0—2 min. In absence of the ion the reactions may take 5—>30 min. N. M. B.

Induced oxidation of oxalic acid by dichromate with ferrous sulphate as inductor. C. R. Viswanadham and G. G. Rao (*Current Sci.*, 1943, 12, 327).—Oxalate (I) interferes with the titration of FeSO_4 with $\text{Na}_2\text{Cr}_2\text{O}_7$, giving results that required for oxidation of Fe^{2+} . In absence of FeSO_4 , (I) is not attacked by $\text{Na}_2\text{Cr}_2\text{O}_7$, and it is concluded that interference of (I) is caused by the rapid reaction of FeSO_4 and $\text{Na}_2\text{Cr}_2\text{O}_7$, inducing reaction between (I) and $\text{Na}_2\text{Cr}_2\text{O}_7$. The induction factor increases with increasing concn. of (I), $[\text{FeSO}_4]$ and $[\text{H}^+]$ being const. FeSO_4 also induces reaction between $\text{Na}_2\text{Cr}_2\text{O}_7$ and tartaric, malic, and citric acid, but not succinic acid. A. T. P.

Interpretation of the Sandmeyer reaction. V. Comparative behaviour of cuprous, cupric, and ferric chlorides as catalysts. H. H. Hodgson and D. D. R. Sibbald (*J.C.S.*, 1944, 393—395).—The catalytic activity of Cu_2Cl_2 , CuCl_2 , FeCl_3 , and $\text{Cu}_2\text{Cl}_2 + \text{CuCl}_2$ for the decomp. of $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-N}_2\text{Cl}$ in HCl has been investigated. With FeCl_3 an almost proportional decrease in yield of $p\text{-C}_6\text{H}_4\text{Cl-NO}_2$ occurs on dilution. Max. are observed with CuCl_2 at 26.9% and 4% of HCl and with Cu_2Cl_2 at 18.6% of HCl . The max. at 4% of HCl suggests the existence of a complex hydrated CuCl_2 anion, in which Cl is much more active than the bound H_2O . C. R. H.

Mechanism of co-polymerisation. T. Alfrey, jun., and G. Goldfinger (*J. Chem. Physics*, 1944, 12, 205—209).—By the aid of steady-state approximation the mechanism of catalytic co-polymerisation of two monomers A and B is discussed on the assumption of two initiation and two termination rates (one for each monomer). Four propagation rates, corresponding with the four possible types of "chain" addition, are considered and overall rates and no. average mol. wt. are calc. The composition of the polymer and the no. distribution curves of groups of sub-mols. are calc. as functions of the monomer composition and two rate const. ratios and are of general character and independent of the nature of the initiation and termination processes if the average degree of polymerisation is "high." W. R. A.

Co-polymerisation of systems of three and more components. T. Alfrey and G. Goldfinger (*J. Chem. Physics*, 1944, 12, 322; cf. preceding abstract).—The authors' method of calculating the course of co-polymerisation in two-component systems is extended to apply to systems of > two components. L. J. J.

Autoxidation of ascorbic acid in presence of vanadic acid, molybdic acid, and tungstic acid sols. S. C. Shome (*J. Indian Chem.*, 1944, 21, 19—23).—At all concns. V_2O_5 sol accelerates and WO_3 sol inhibits the autoxidation of ascorbic acid. MoO_3 sol accelerates autoxidation at low and inhibits it at high concns. C. R. H.

Oxidation processes. XVII. Autoxidation of ascorbic acid in presence of copper. A. Weissberger and J. LuValle (*J. Amer. Chem. Soc.*, 1944, 66, 700—705; cf. A., 1944, I, 42).—The rate of

autoxidation of ascorbic acid (I) in presence of Cu at pH 2.59—9.31 is $\propto [\text{O}_2]$ and independent of concn. of (I). At very low [Cu] it increases faster than the [Cu], but is $\propto [\text{Cu}]$ at higher [Cu]. The effect of pH shows that only the univalent ion of (I) is the substrate of Cu catalysis, but the effects may appear complex owing to interaction of some buffers with the Cu. The primary reaction is formation of 1 mol. each of dehydroascorbic acid and H_2O_2 from 1 mol. each of (I) and O_2 . The reaction mechanism is discussed. Ag has no effect. R. S. C.

Stepwise activation of oxygen in the organism.—See A., 1944, III, 611.

Mechanism of the oxidation of sulphur dioxide on active vanadium catalysts. I. Stability of single vanadium compounds in the conditions of the synthesis of sulphuric acid. G. K. Borcskov and V. P. Pligunov (*J. Appl. Chem. Russ.*, 1940, 13, 329—336).— V_2O_5 (I), $\text{V}_2\text{O}_5 + 0.1 \text{ K}_2\text{SO}_4$ (II), $\text{V}_2\text{O}_5 + 0.1 \text{ K}_2\text{O}$ (III), $\text{V}_2\text{O}_5 + 0.5 \text{ K}_2\text{O}$ (IV), $\text{V}_2\text{O}_5 + 0.9 \text{ K}_2\text{O}$ (V), $\text{V}_2\text{O}_5 + 1.0 \text{ Na}_2\text{O}$ (VI), $\text{V}_2\text{O}_5 + 1.0 \text{ BaO}$ (VII), $\text{V}_2\text{O}_5 + 0.9 \text{ K}_2\text{O} + 1.9 \text{ SiO}_2$ (VIII), $\text{V}_2\text{O}_5 + 0.9 \text{ K}_2\text{O} + 7.7 \text{ SiO}_2$ (IX), and $\text{V}_2\text{O}_5 + 0.9 \text{ K}_2\text{O} + 38.4 \text{ SiO}_2$ (X) have been heated for 12—16 hr. at 480° in air + 5% of SO_2 + 5% of SO_3 . V_2O_5 was partly reduced to V_2O_4 (probably as VOSO_4), and the degree of reduction increased in the order (X) < (I) < (IX) < (V) < (VI) < (VIII) < (II), (III), (IV), (VII), the reduction being complete for (II) etc. BaO was converted into BaSO_4 , and Na_2O , K_2O , and K_2SO_4 gave pyrosulphates. The results disagree with Neumann's theory (B., 1935, 898). J. J. B.

Metal-catalysed reaction between acetylene and hydrogen. I. Nickel catalysts. J. Sheridan (*J.C.S.*, 1944, 373—380).—A nearly linear pressure-time curve is usually obtained for the first stages of the reaction between H_2 and C_2H_2 in presence of Ni catalyst. The fall in pressure becomes slower towards the end of the reaction. The activity of the catalysts increases markedly in the early stages of the reaction, then becoming steady over considerable periods. The yields of C_2H_4 , C_2H_6 , and higher hydrocarbons (empirically $\sim \text{C}_4\text{H}_8$) are the same on fresh and old catalysts, and so the increase in activity of the catalyst at the beginning of the reaction is not specifically in favour of a particular type of reaction in the system. The production of C_2H_4 is ~ 5 times that of C_2H_6 . The yield of " C_4H_8 " is 55—60% of the unrecovered C_2H_2 at all stages of the reaction. The data indicate that the kinetics of C_2H_4 and C_2H_6 formation and of " C_4H_8 " formation are the same, being first order with respect to H_2 and approx. zero order with respect to C_2H_2 . The data are discussed with reference to earlier work on chemisorption of C_2H_4 and C_2H_2 . C. R. H.

Use of palladium and platinum as catalysts.—See B., 1944, I, 315.

Possible use of palladium as catalyst in manufacture of acrichine.—See B., 1944, II, 245.

Action of carbonate catalysts in carburisation of steel.—See B., 1944, I, 313.

Influence of lead and manganese as driers in oil paints.—See B., 1944, II, 290.

Liberation of iodine from dilute iodide solutions by electrolysis on a monolithic porous carbon electrode. II. E. N. Vinogradova (*J. Appl. Chem. Russ.*, 1940, 13, 390—393).—A solution containing per l. 150 g. of NaCl, 0.05 g. of I⁻, and small amounts of other ions is filtered through an electrode made of active C, towards an Fe cathode. The voltage applied is 5 v. at the beginning, and 2 v. in the steady state of the electrolysis; if it is too high, IO_3^- is formed, and at <1.5 v. I⁻ is not completely discharged. I_2 formed is adsorbed by the C. Through 10 sq. cm. of the electrode surface 500 c.c. per hr. can be passed without losing >1% of I. The method is recommended for recovery of I from oil well H_2O . J. J. B.

Formation of oxide layers on aluminium, especially on the anodes of electrolytic condensers. W. Hermann (*Kolloid-Z.*, 1943, 102, 113—127).—Modifications of Al_2O_3 are described and discussed. It is possible to find a common structural basis for the formation of the various types of oxide layer. The foundation of all Al_2O_3 layers is a film of $\gamma\text{-Al}_2\text{O}_3$, or a variety of it. Al^{3+} can migrate from the Al below, through the empty spaces in the spinel lattice of the $\gamma\text{-Al}_2\text{O}_3$. The film grows on the outer surface by reaction between Al^{3+} and O_2 or the anions of the electrolyte. In the case of the film formed in O_2 at room temp., there is a very thin layer embedded in one of greater thickness. By anodic treatment in suitable electrolytes, particularly aq. or alcoholic boric acid or borates, the layer may assume a thickness of 0.7 μ . The dielectric film grows only if the field strength is >10 mv. per cm. When a certain film thickness has been reached the field distribution curve in the Al_2O_3 slopes so steeply that electrons can penetrate the film with production of sparks. The sparking potential depends on the ionic concn. or conductivity of the electrolyte. In some electrolytes, e.g., H_2SO_4 , $\text{H}_2\text{C}_2\text{O}_4$, and H_2CrO_4 , a thick porous layer of Al_2O_3 is formed in addition to the thin dielectric film. A. J. M.

Behaviour of positive plates with lead-calcium alloy grids in lead accumulators.—See B., 1944, I, 315.

Lead plating.—See B., 1944, I, 314.

Use of palladium and platinum for electro-coatings.—See B., 1944, I, 315.

Photochemical processes in aromatic compounds. A. Terenin (*Acta Physicochim. U.R.S.S.*, 1943, 18, 210—241).—The main results obtained in earlier photochemical investigations are reviewed in order to arrive at a consistent picture of photochemical mechanisms. Many of the facts established for gaseous aromatic compounds have been explained on the assumption of a definite shape for the potential energy surfaces of the ground and excited states and of the existence of a definite angle between their principal sections. Evidence is given for the existence of a long-lived metastable electronic state in simpler derivatives of C_6H_6 in the gaseous and liquid states at low temp., which state may correspond with a triplet term of the aromatic ring. The connexion between the emission spectra of these derivatives at low temp. and their polymerisation processes is accounted for. Reaction mechanisms of O_2 with aromatic mols. are discussed from the viewpoint of conservation of the electronic spin. C. R. H.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Exchange reactions. R. Daudel (*Compt. rend.*, 1943, 216, 666—667).—Two main types of exchange reaction can be distinguished. In some cases an exchange of free, radioactive A^* for inactive A in the inactive compound AB takes place. There is a continual dissociation of AB into its elements. Thus, $AB \rightleftharpoons A + B$, $A^* + B \rightleftharpoons A^*B$, or, together $AB + A^* \rightleftharpoons A^*B + A$. The reaction is very rapid when the elements A and B are of opposite electrochemical character, and in aq. solution. The other type occurs through the formation of an intermediate mol. If AB and A^*C are the two reacting mols., $AB + A^*C \rightleftharpoons AA^*BC \rightleftharpoons A^*B + AC$. This type can be sub-divided into two, according as AA^*BC is, or is not, capable of isolation. Applications of this classification are mentioned. A. J. M.

Polymerisation with atomic hydrogen. J. P. W. Houtman, K. van den Berg, and P. M. Heertjes (*Rec. trav. chim.*, 1943, 62, 672—680).—Chemical affects of "atomic" H are uncertain unless the method of production ensures the absence of excited atoms, ions or electrons. The Langmuir thermal method is shown to produce ions; these are completely removed for $p > 0.4$ mm. by two metal plates between which is a p.d. of 10 v. The photochemical method, using a Hg sensitiser, gives only unexcited H atoms for $\lambda > 2300$. Using H from Langmuir's method hexadecene was polymerised and the polymerisation shown to be independent of the presence of ions by variation of the p.d. between the plates. Using H from the photochemical method WO_3 gave W and linseed oil was hydrogenated and polymerised. On a large scale, linseed oil was hydrogenated and polymerised and hexadecene reduced to hexadecane and a polymerised reduction product. All experiments were repeated using N_2 as the gas present to verify that the activity was due to H. J. O'M.B.

Action of non-metals on basic oxides. M. Lemarchand and L. Schwartz (*Compt. rend.*, 1942, 214, 982—983).—The action of S on Ag_2O has been investigated by examining the direct action of S vapour on the surface of Ag_2O for a long period (up to 96 days) and at different temp., and by shaking a solution of S in CCl_4 with Ag_2O for several weeks. An additive compound, Ag_2OS , is formed. It is steel-grey, has d 6.08, and is insol. in H_2O . It dissociates when heated (300—350°) into Ag_2S and Ag_2SO_3 . H_2 at 170° is without action. CO reduces it quantitatively to Ag_2S . It differs from Ag_2O and Ag_2S in its X-ray spectrum and its mol. vol. (Ag_2O 32.2, Ag_2S 34.1, Ag_2SO_3 43.4). A. J. M.

Preparation of copper phosphides by electrolysis of melts. M. Chène (*Compt. rend.*, 1942, 214, 977—979; 215, 81—83).—Electrolysis of fused Na metaphosphate containing varying amounts of dissolved Cu_2Cl_2 or CuO gives cryst. Cu phosphides, together with Cu at the cathode. Cu_3P and Cu_2P were isolated. Cu_3P , dark grey, has d^{20} 7.09. Cu_2P , dark brown, has d^{20} 5.51. Both are oxidised in warm air, are slowly attacked by HCl, and reduce warm conc. H_2SO_4 . When heated, Cu_2P readily evolves P, which ignites. A. J. M.

Fusion process in non-polar crystals. II. Explanation of mercury corrosion figures on copper crystal spheres. I. N. Stranski (*Naturwiss.*, 1943, 31, 144—145).—Spheres cut from Cu single crystals show typical corrosion figures when acted on by Hg and HNO_3 . The effect of Hg on the surface will be very similar to the fusion process. Rhombododecahedral areas of the Cu become covered with Hg and the thin "lanes" separating these areas retain their Cu colour. The phenomenon is explained on the basis of density of packing in the various surfaces of the Cu crystal. A. J. M.

Behaviour of aluminium in the etching of crystal figures. H. Mahl and I. N. Stranski (*Naturwiss.*, 1943, 31, 12—17).—The theory

of the etching of non-polar and ionic crystals is discussed. In the case of Al, in the absence of O_2 , e.g., in etching by means of dry HCl gas, octahedra in combination with cubes are obtained, as required by theory. In the presence of O_2 , the etching figures are those of the oxide layer on the surface, with an ionic lattice. In etching with HCl or electrolytically, the pure cube form is obtained, due to a two-dimensional oxide layer on the Al, of NaCl type. A. J. M.

Crystal structure [and preparation] of $ZnSb_2O_4$ and isomorphous compounds.—See A., 1944, I, 216.

Derivatives of monosilane. III. Fluoromonosilanes. H. J. Emeléus and A. G. Maddock (*J.C.S.*, 1944, 293—296).—Interaction of $SiHCl_3$, SiH_2Cl_2 , and SiH_3Cl with SbF_5 at room temp. in presence of $SbCl_5$ yields $SiHF_3$, silylene fluoride SiH_2F_2 , and silyl fluoride SiH_3F , respectively, the max. yields obtained being 91%, 80%, and 79% respectively. The v.p. for various temp. < b.p. are recorded and the following physical consts. have been determined: m.p. $SiHF_3$ —131.4°, SiH_2F_2 —122°; b.p. $SiHF_3$ —95.0°, SiH_2F_2 —77.8°, SiH_3F —98.6°; latent heat $SiHF_3$ 4802, SiH_2F_2 4751, SiH_3F 4500 g.-cal. per mol. Attempts to prepare SiH_2F_2 and SiH_3F by interaction of SiH_4I_2 and SiH_3I with AgF or HgF were unsuccessful. All these compounds undergo disproportionation at room temp. with formation of SiH_4 and SiF_4 , although with SiH_2F_2 decomp. is slow. The anomalous b.p. and Trouton's consts. indicate association in the liquid phase attributable to H-bonds. J. W. S.

Preparation of hypophosphoric acid and its sodium salt, $Na_2H_2P_2O_6 \cdot 6H_2O$. W. Jung (*Anal. Assoc. Quím. Argentina*, 1942, 30, 99—111).—A detailed description of the prep. and purification of $Na_2H_2P_2O_6$ by Blaser and Halpern's (A., 1934, 43) modification of Corne's method. The yield is improved. F. R. G.

Preparation of alkali tungstates in the dry way. E. Carrière, H. Guiter, and R. Giacomini (*Bull. Soc. chim.*, 1943, [v], 10, 587—588).—The action of WO_3 on alkali carbonates and sulphates at elevated temp. gives salts of the type $WO_3 \cdot pM_2O$, where p depends on the proportions used. Using excess of Li_2CO_3 , the compound $WO_3 \cdot 2Li_2O$ was obtained. In each case the min. temp. of reaction was determined, the carbonates being more readily attacked than the sulphates. J. F. H.

Composition and mechanism of formation of the hydrides of nickel. II. Reaction mechanism. A. A. Balandin, B. V. Jerofoev, K. A. Pecherskaja, and M. S. Stachanova (*Acta Physicochim. U.R.S.S.*, 1943, 18, 300—310).—Weichselder's view that the formation of NiH_2 from $NiCl_2$, $MgPhBr$, and H_2 is due to the interaction of H_2 with $NiPh_2$, formed as an intermediate compound, is incorrect. $NiCl_2$ is reduced to Ni by $MgPhBr$ in absence of H_2 . The formation of Ni hydrides by interaction of reduced Ni and H_2 proceeds in stages. These stages are autocatalytic, the dissolved H_2 reacting with solid Ni and with the hydrides and NiH , NiH_2 , and NiH_4 are formed. The Ni surface is poisoned by certain strongly adsorbed compounds, e.g., thiophen, which prevent the penetration of H_2 to the Ni surface and formation of hydride. The poisoning effect is even greater for catalytic hydrogenation of the C_6H_6 nucleus; on the other hand, the poisoning effect on the dissolution of H_2 in the hydrides is very small. Sols of Ni hydrides in Et_2O and other solvents were examined. Those in Et_2O are less stable than those in C_6H_6 , PhMe, and xylene. Colloidal solutions in Et_2O are formed only when $[MgPhBr]$ is $> 0.5M$, suggesting that adsorption of $MgPhBr$ on the hydride surface protects the colloid. H_2O and air rapidly coagulate the sols. C. R. H.

XI.—GEOCHEMISTRY.

Iodine-air investigations. H. Jesser and E. Thomae (*Z. anal. Chem.*, 1943, 125, 89—93).—Data showing the I content of the atm. over Stuttgart during the year 1941 are recorded and discussed. The vals. found are < those reported for previous years (A., 1939, I, 391). L. S. T.

Magnesium content of rain-water at Grignon. G. Bertrand (*Ann. Inst. Pasteur*, 1943, 69, 294—302).—In rain- H_2O collected during 1 year it is calc. that, of every 100 g. of Mn, only 0.0122 g. could not be accounted for as contamination from dust or other sources. F. S.

Magnesium and calcium in rain-water collected at Paris. G. Bertrand (*Compt. rend.*, 1943, 216, 701—704).—Even when care was taken to prevent dust from being collected with the rain- H_2O , it was found that in rain collected over 1 year, a deposit of ~0.8 g. of mineral matter was obtained on evaporation. This contained Mg and Ca salts. A. J. M.

Lakes and wells of Kustanai region. V. D. Poljakov and D. I. Kusnetsov (*J. Appl. Chem. Russ.*, 1940, 13, 404—411).—Some lakes near Kustanai (Western Siberia) contain deposits of $Na_2SO_4 \cdot 10H_2O$ and of other minerals. J. J. B.

Zinc-polluted River Ystwyth, north Cardiganshire, Wales. J. R. E. Jones (*Ann. Appl. Biol.*, 1940, 27, 368—378).—A survey of the

river which flows through areas of disused Zn mine workings is recorded. At normal level the H_2O contains 0.7—1.2 mg. of Zn and >0.05 mg. of Pb per l. The flora and fauna of the river are described. A. G. P.

Nature and significance of certain variations in composition of Los Angeles basin ground waters. R. R. Morse (*Econ. Geol.*, 1943, 38, 476—511).—Comparison of the numerous chemical analyses recorded shows the presence of several distinctive types, and indicates that different processes of varying importance operate to produce chemical variation. The occurrence and general relationships of the H_2O types are discussed. L. S. T.

Photometric study of the coloration of sulphuric acid by organic compounds of [sea-]water. V. G. Datzko (*J. Appl. Chem. Russ.*, 1940, 13, 384—389).—The H_2O of Caspian Sea darkens conc. H_2SO_4 ~10 times as much as does ocean H_2O near Greenland. The degree of coloration is a measure of the admixture of river- H_2O to the sea- H_2O (see C., 1944, Part 4). J. J. B.

Migration of substances in the earth's crust. C. W. Correns (*Naturwiss.*, 1943, 31, 35—42).—A review. The composition of the earth's crust is discussed. Processes causing migration of substances are distinguished as weathering, the formation of sediments from the weathering products, metamorphosis of rocks, and volcanic action. The part played by organisms in the formation of sediments is discussed. A. J. M.

Effect of a thin superficial deposit [of Fe] on the magnetisation of a steel ball. Application to magnetic properties of rocks. (Mme.) F. Bayard-Duclaux (*Compt. rend.*, 1943, 216, 727—728).—The effect of depositing Fe on a steel ball on its intensity of magnetisation (I) has been investigated. I reaches half its initial val. when a layer of Fe equal to 0.036 of its radius has been deposited. The deposited Fe acts as a magnetic screen. The magnetisation of volcanic rocks is stable for unaltered rocks, but is variable for altered ones. The above experiments show that if the magnetism of the rock is due to grains of magnetite or more complex Fe compound, alteration of the surface would create a new ferromagnetic layer, which would considerably affect the magnetic properties of the interior. A. J. M.

Application of radio-chemical analysis for the correlation of geological strata. V. I. Baranov, K. G. Kunasheva, and S. G. Zeitlin (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 178—190).—Cores from test oil borings in the Kazan area were examined. The cores were from the lower Permian and upper Carboniferous strata. The average concn. of Ra in the cores was $5.38 \times 10^{-11}\%$ and of Th $1.09 \times 10^{-10}\%$. Well-waters examined had [Ra] of the same order. V. B.

Diamonds in the north-eastern Bolivian Andes. V. Oppenheim (*Econ. Geol.*, 1943, 38, 658—661).—Diamonds have been found in the river gravels of Rio Tuichi. Origin is discussed. L. S. T.

Quartz crystal in New Zealand. J. Henderson (*New Zealand J. Sci. Tech.*, 1944, 25, B, 162—169).—Properties and uses of quartz crystal, and occurrences in New Zealand, are described. South Westland and Takaka appear to be the districts in which crystals suitable for piezo-electrical purposes may be found. L. S. T.

Melting and crystallisation of rock-forming minerals. J. F. Schairer (*Amer. Min.*, 1944, 29, 76—91).—A survey that shows the progress made in determining the chemical compositions, range of compositions, and the temp.—stability relationships of the various rock-forming olivines, pyroxenes, and melilites. Relevant equilibrium diagrams are reproduced. L. S. T.

Crystallography of calcite from Lake Superior copper mines. C. Palache (*Amer. Min.*, 1944, 29, 35—48).—Crystallographic forms are tabulated and illustrated. L. S. T.

Brucite in limestone near Wilkinson, Ontario. I. C. Brown (*Econ. Geol.*, 1943, 38, 408—419).—Brucite (I) is present as granules, blades, and needles disseminated in magnesian limestone at Wilkinson. It has formed at the expense of dolomite (II), the Ca of (II) going to form calcite. (I) from Wilkinson contains no remnants of periclase, and is regarded as the result of a process in which H_2O replaced CO_2 of (II). Chemical analyses are recorded. L. S. T.

Calcite-dolomite staining tests. W. S. T. Smith (*Econ. Geol.*, 1943, 38, 420—422).—Results described for distinguishing dolomite from calcite in the ore deposits of the Joplin region show that the hamatoxylin and the $FeCl_3$ staining methods are untrustworthy for these deposits. L. S. T.

Deposit of barite and fluorspar, Thomson Hill, Wangapeka survey district, Nelson. E. O. Macpherson (*New Zealand J. Sci. Tech.*, 1944, 55, B, 178—180).—The deposit is described, and chemical analyses are given. L. S. T.

Distribution of helium and radioactivity in rocks. VI. The Ayer granite-migmatite at Chelmsford, Mass. N. B. Keevil, E. S. Larsen, and F. J. Wank (*Amer. J. Sci.*, 1944, 242, 345—353; cf. A., 1944,

I, 46).— >20 samples of rock and mineral concentrates from the Chelmsford granite-migmatite have been investigated. A wide range of radioactivities is shown by the 12 mineral concentrates; zircon (I), apatite, epidote, and biotite have >5 times the radioactivity of the parent rock. A 10,000-fold contrast in activity and a 150,000-fold contrast in He content were found between (I) and feldspar (II); the (II), containing 1.2 c.c. per g., appears to retain He, whilst the (II) and quartz have lost $>90\%$. Excess He over that produced since Carboniferous time was found in sphene. $>50\%$ of the radioactivity of the Chelmsford granite is due to accessory minerals. L. S. T.

Distribution and conditions of the primary migration of radioelements in nature. I. E. Starik (*Uspechi Chim.*, 1943, 12, 287—307).—Occurrence of radioactive elements in igneous and sedimentary rocks, rate of diffusion of gaseous and solid elements in the rocks, migration of these elements in the rock fissures, and related phenomena are discussed. J. J. B.

Thorium-uranium ratios in rocks and minerals. N. B. Keevil (*Amer. J. Sci.*, 1944, 242, 309—321).—100 recent determinations, including new data, of these ratios are tabulated, and plotted as frequency-distribution curves. The probable val. of Th/U for an igneous rock lies between 3.0 and 3.5. Independent confirmation of this range is given by Nier's determinations of abundances of Pb isotopes from samples of ore-Pb. For most purposes a val. of 3.2 can be assumed for the Th/U ratio. This leads to no significant error in α -counting theory and in determinations of the rate of production of radiogenic heat or of accumulation of He and Pb in rocks. The results do not support Holmes' theory of the genesis of Pb ores from a deep-seated source. L. S. T.

Dissolution of astrakhanite salt root in salt solutions. V. I. Nikolaev and N. A. Ilinich (*J. Appl. Chem. Russ.*, 1940, 13, 394—403).—Astrakhanite salt root is a deposition of minerals (astrakhanite, epsomite, and rock-salt) which has grown through the mud bed of many salt lakes near the delta of Volga. The dissolution of this mixture in some salt solutions without stirring shows rhythmic changes. At an undisturbed dissolution in a salt lake the upper layer of liquid contained mainly NaCl, the middle one mainly $MgSO_4$, and the lower one $MgSO_4$ and Na_2SO_4 . Astrakhanite forms no solid solutions either with epsomite or with rock-salt. J. J. B.

Structure of natrophilite, $NaMnPO_4$.—See A., 1944, I, 216.

Composition of some chromites of the Western Hemisphere. R. E. Stevens (*Amer. Min.*, 1944, 29, 1—34).—52 complete and 144 partial chemical analyses of purified chromites (I) from different deposits in the Western Hemisphere are recorded and discussed. The composition of (I) is represented by $(Mg,Fe)O \cdot (Cr,Al,Fe)_2O_3 \cdot Fe_2O_3$ is generally present, frequently as a minor, and commonly as a major, constituent. Terrestrial (I) are predominantly magnesio-(I) $MgO \cdot Cr_2O_3$ (II), hence ferro-(I), $FeO \cdot Cr_2O_3$ (III), is not the ideal formula for (I). The end members (II), (III), spinel (IV), hercynite, magnesio-ferrite, and magnetite (V) occupy the corners of a triangular composition prism. The principal zone of isomorphism for the (I) in this prism ranges from compositions approaching (II) and (IV) to (V), leading to the division of (I) into the following types, with the replaceable ions given in order of abundance: aluminian chromite $(Mg,Fe)O \cdot (Cr,Al,Fe)_2O_3$; ferrian chromite, $(Mg,Fe)O \cdot (Cr,Fe,Al)_2O_3$; chromian-spinel $(Mg,Fe)O \cdot (Al,Cr,Fe)_2O_3$; ferrian-spinel $(Mg,Fe)O \cdot (Al,Fe,Cr)_2O_3$; chromian-magnetite $(Fe,Mg)O \cdot (Fe,Cr,Al)_2O_3$; and aluminian-magnetite $(Fe,Mg)O \cdot (Fe,Al,Cr)_2O_3$. Data showing the variation of unit-cell edge with Cr content, and the no. of atoms of Cr, Al, Fe^{2+} , Fe^{3+} , and Mg per unit cell in order of increasing Fe^{3+} , are recorded. L. S. T.

Colloidal deposition of cinnabar. J. Pollock (*Amer. Inst. Min. Met. Eng.*, 1944 *Tech. Publ.* 1735, 10 pp.; *Min. Tech.*, 8, No. 4).—The stability of HgS sols (0.01—2.0 g. per l.) has been studied at room temp. The Schulze-Hardy rule is roughly obeyed ($Na^+ : Ca^{++} : Al^{+++} = 1 : 50 : 625$), and the stability of the sol increases with pH. The flocculation time in 0.035M-NaCl increases slowly with decreasing [HgS] down to vals. of ~ 0.06 g. per l., below which the flocculation time is infinite. SiO_2 sols have a strongly protective action, the flocculation time becoming infinite at $SiO_2 : HgS > 3 : 1$; at this val. the system behaves essentially as a SiO_2 sol. HgS is stable as a sol in natural H_2O known to be depositing cinnabar (I), and deposits containing finely-divided (I) (especially opalite) have probably derived it from colloidal solution. M. H. M. A.

Tungsten deposits of Southern Kiangsi, China. K. C. Hsu (*Econ. Geol.*, 1943, 38, 431—474).—Mode of occurrence of the deposits, the nature of the ore bodies, sequence of mineralisation, and some of the important districts are described. The Kiangsi deposits supply $\sim 70\%$ of the total output of Chinese W concentrates. Most of the deposits are hypothermal veins, but some are pegmatitic. The veins occur in granite and in sedimentary rocks not far from the granite intrusives. Greisenisation without development of topaz and tourmaline is the usual type of wallrock alteration in granite. Tourmalinisation is a common type of alteration in argillaceous

sediments near the veins. Wolframite is the chief ore mineral, whilst cassiterite, Bi minerals, molybdenite, and chalcocypite are of local economic importance. L. S. T.

Tungsten deposits of the Darwin Hills, Inyo Co., California. L. K. Wilson (*Econ. Geol.*, 1943, 38, 543—560).—The general geology of the district, and the mineralogy, origin, and extent of the scheelite ore-bodies, are described. L. S. T.

Manganese deposits of the Turtle mountains, N. Dakota. T. A. Hendricks and W. M. Laird (*Econ. Geol.*, 1943, 38, 591—602).—The chief Mn spring deposits of this locality have been investigated. Mineral Spring contains ~16,000 tons of Mn ore as rancieite (I) in calcareous tufa with a Mn content of ~10%. The source of the Mn appears to be in Mn limonitic concretions. Chemical analyses are recorded. (I) is probably $(\text{Ca}, \text{Mn}^{II})\text{Mn}^{IV}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. L. S. T.

Boron in braunite and manganese ores. B. Wasserstein (*Econ. Geol.*, 1943, 38, 389—398).—Spectrographic determinations of B_2O_3 in Mn ores are recorded and show that B (~0.5—1%) is a const. constituent of braunite (I), but not necessarily of other Mn minerals. The presence of B in (I) is considered to be due to isomorphous replacement of Si in the crystal lattice. L. S. T.

Pyrolusite. H. Strunz (*Naturwiss.*, 1943, 31, 89—91).—The optically and morphologically rhombic naturally occurring MnO_2 is tetragonal in agreement with its known rutile-like form, but occurs in submicroscopic crystallites pseudomorphous with other minerals, particularly manganite. The rhombic pseudomorphism is a "relict effect." L. J. J.

Colloform sulphide veins of Port au Port peninsula, Newfoundland. K. de P. Watson (*Econ. Geol.*, 1943, 38, 621—647).—Colloform deposits of Pb, Zn, and Fe sulphides are described, and their origin is discussed. L. S. T.

Low-chalcocite and high-chalcocite. M. J. Buerger and N. W. Buerger (*Amer. Min.*, 1944, 29, 55—65).—Bristol chalcocite (I) has been investigated by the Weissenberg and by the de Jong-Bouman methods. (I), orthorhombic, diffraction symbol $mmmAb-$, has a_0 11.90, b_0 27.28, c_0 13.41 Å. The Weissenberg investigation of high-(I) [Bristol (I) maintained above the inversion temp. of 105°], shows high-(I) to be hexagonal, with a diffraction symbol $6/mmmH6/-c-$, and a_0 3.89, c_0 6.68 Å. The low-(I) cell bears a super-cell relation to the high-(I) cell; its a , b , and c axes are 3, 4, and 2 times, respectively, those of the high-(I) cell. Space-groups are $H6mcm$ ($D_{6h}4$) for high-(I), and $Ab2m$ ($C_{2v}15$) for low-(I). L. S. T.

Weinschenkite, yttrium phosphate dihydrate, from Virginia. C. Milton, K. J. Murata, and M. M. Knechtel (*Amer. Min.*, 1944, 29, 92—107).—Weinschenkite (I), previously known only from one Bavarian locality, occurs at Kelly Bank mine, Vesuvius, Virginia. (I) from Virginia has a 1.605, b 1.612, c 1.645, ρ_{calc} 3.270, ρ_{obs} 3.263. X-Ray data are recorded. Spectrograms of (I) from Virginia and from Bavaria are practically identical; the Yb lines are stronger in the Virginian mineral. Lines due to Ti, As, Ag, Bi, Cd, Pb, Sb, Sn, Zn, Cu, Ba, Sr, B, Be, and Ge are absent. Major elements present are Y, Yb, Er, Dy, and Gd, minor elements are Nd, Sm, Eu, Ho, and La (trace); Th, Sc, Ce, Pr, Tb, and Lu were not found. (I) and artificially-prepared $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$ show a moderately strong pink fluorescence (Hg-vapour lamp) when heated gently; on strong ignition, fluorescence ceases. $14 \text{ H}_2\text{O}$ are lost at 180°, and $2\text{H}_2\text{O}$ at 900°. Origin of (I) is discussed. L. S. T.

Magnetic behaviour of a tektite. A. Sigamony (*Proc. Indian Acad. Sci.*, 1944, 20, A, 15—17).—A sample of tektite from the island of Billiton has ρ 2.448, χ 7.78×10^{-8} at 25°, and is magnetically isotropic. From χ the estimated FeO content is 5.8% in agreement with the known structure and composition of tektites. W. R. A.

Radium content of Ceylon thorianite. P. K. S. Chaudhury (*Indian J. Physics*, 1943, 17, 257—261).—A sample of Ceylon thorianite contained $\sim 5.94 \times 10^{-8}$ g. Ra per g. W. R. A.

Structure and colour reactions of montmorillonite earths. D. Krüger and F. Oberlies (*Naturwiss.*, 1943, 31, 92).—A variety of natural earths which show a feeble benzidine reaction in their natural state show a marked positive benzidine reaction after drying in vac. at room temp. or at 100° at atm. pressure. Hence factors other than lattice or chemical structure are operative in this reaction. The effect is ascribed to irreversible dehydration of SiO_2 or Al_2O_3 gel components. The nature of the exchangeable cations present also affects the reaction. L. J. J.

Determining factors in the coloration of granite soils in the south-eastern Piedmont. W. A. White (*Amer. J. Sci.*, 1944, 242, 361—363).—By its control of internal drainage, jointing also controls the alternation of oxidising and reducing conditions in the soil. Red soils develop on closely-jointed granites because of the good internal

drainage and the oxidising conditions that prevail. Yellow soils develop on sparsely-jointed granites where internal drainage is poor and reducing conditions mainly prevail. L. S. T.

Geology of the manganiferous iron ore deposits at Boston Hill, New Mexico. L. P. Entwistle (*Amer. Inst. Min. Met. Eng.*, 1944, 8, *Tech. Publ.*, 1712, 10 pp.).—The hypogene mineralisation of the intrusion carrying the Mn ores consists of three stages: the formation of (1) mesitite, a Mn Fe magnesite, (2) quartz and sulphides, and (3) barite-galena. The hypogene carbonate has been oxidised and enriched by meteoric waters containing excess of O_2 and CO_2 to form ore bodies of intimately mixed hæmatite and pyrolusite. L. S. T.

System Fe_2O_3 — Mn_2O_3 . Comments on the names bixbyite, sitaprite, and partridgeite. B. Mason (*Amer. Min.*, 1944, 29, 66—69).—The phase diagram for the system Fe_2O_3 — Mn_2O_3 is reproduced and discussed. It shows that max. replacement of Mn by Fe is ~30% at 600°, increasing rapidly with a rise in temp. to ~60% at 1000°. The mineral $(\text{Fe}, \text{Mn})_2\text{O}_3$ can be subdivided into two groups to include (i) minerals of pneumatolytic or fumarolic origin with 40—60% of Fe_2O_3 , and (ii) those occurring in metamorphosed Mn ores, with 0—30% of Fe_2O_3 . The name bixbyite covers the $(\text{Fe}, \text{Mn})_2\text{O}_3$ group satisfactorily, but if the group is to be subdivided, it should be into bixbyite, corresponding with sub-group (i), and sitaprite, corresponding with sub-group (ii). The name partridgeite is unnecessary (cf. A., 1944, I, 92). L. S. T.

Hydrothermal replacement in deep-seated iron ore deposits of the Lake Superior region. T. T. Quirke (*Econ. Geol.*, 1943, 38, 662—666).—A discussion (cf. A., 1943, I, 243). L. S. T.

Chemical and mineralogical composition of twenty typical "limonites." R. Blanchard (*Amer. Min.*, 1944, 29, 111—114).—Chemical analyses and calc. probable mineralogical compositions of 20 typical limonitic products of diverse origin and distribution are recorded and discussed. In spite of the typical limonitic appearance of all the hand specimens, wide variations in the composition, extent, and nature of the impurities present exist. The analyses also show that $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ may and often does exist in porous gossans with too low a content of adsorbed and capillary H_2O to conform to the theoretical formula, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, formerly assigned to limonite. L. S. T.

Bravoite from a new locality. C. A. Rasor (*Econ. Geol.*, 1943, 38, 399—407).—Bravoite, $(\text{Ni}, \text{Fe})\text{S}_2$, has been identified as a constituent of the Ni—Co ores of south-eastern Missouri. L. S. T.

Cobalt content of some South Island (New Zealand) limestones. D. J. Stanton (*New Zealand J. Sci. Tech.*, 1944, 25, A, 221—224).—Limestones from the Nelson District contain 0.2—4.2 p.p.m., but generally <2.5 p.p.m., of Co; and those from Southland, Otago, Canterbury, and Marlborough, from 0.2 to 12.5 p.p.m., but generally <5 p.p.m. There appears to be no correlation between geological age and Co content, or between carbonate and Co contents, although high carbonate usually accompanied low Co content. Most South Island limestones are too low in Co to provide useful amounts of Co for top-dressing pastures for the control of Co-deficiency disease in stock. L. S. T.

Mechanism and environment of gold deposition in veins. W. H. White (*Econ. Geol.*, 1943, 38, 512—532).—A study of ores from 27 districts representing the main types of Au deposits in Canada and the United States reveals a no. of characteristic features, some of which are common to most of the deposits. The process of cataclasis, one of minute fracturing and almost contemporaneous recrystallisation of quartz (I) in Au veins, is probably an important factor permitting the residual solutions carrying the Au in the veins to permeate the (I) and distribute the Au. Vacuoles are common in vein (I), and play a part. Au was the last mineral to crystallise, its closest sulphide associate being galena, and occasionally, stibnite, realgar, and cinnabar. It was deposited under uniform conditions of low and waning stress at a temp. possibly <200°. L. S. T.

Alkali sulphide theory of gold deposition. F. G. Smith (*Econ. Geol.*, 1943, 38, 561—590).—It is postulated that natural solutions that deposit primary Au ores contain alkali sulphide, and that the Au is transported as alkali thioaurite. The synthesis of electrum by heating aq. Na_2S saturated with H_2S , Au_2S_3 , and Ag_2S in an atm. of H_2S to ~300°, and allowing cooling to take place in ~12 hr., is described. Calaverite has been synthesised by heating Na_2S_2 with Au and Te; it is formed in alkali sulphide systems only when the concn. of free S is low. L. S. T.

Silicates and dusts from the Witwatersrand gold mines. J. J. Frankel (*J. Chem. Met. Soc. S. Africa*, 1944, 44, 169—177).—Chemical and spectrographic analyses, and X-ray diffraction patterns, of the sericite, pyrophyllite, chlorite, actinolite, epidote, chloritoids, and clay minerals, and X-ray diffraction patterns of the dusts, are reproduced. L. S. T.

Structure of rhodizite.—See A., 1944, I, 240.

A I—General, Physical, and Inorganic Chemistry.

DECEMBER, 1944.

I.—SUB-ATOMICS.

Effect of electrical field strength on the intensities of the lines of the p, p -series of the He I and Li I spectra. R. Siksnas (*Naturwiss.*, 1943, 31, 169—170).—The effects of electrical field strength (F) on the intensities (I) of the lines of the $2p$ — np series of the α -He I spectrum are summarised. I for individual lines increases at first with increasing F , reaches a max. for a definite F , and then decreases. The increase is more rapid than the decrease. Each line has a definite range of F for which it is visible. With increasing term no. the max. intensity (I_{\max}) of the line is less, and the range of F over which it is visible is smaller; also, the F necessary to reach I_{\max} is smaller. If F_m is the field strength necessary to reach I_{\max} for the m th line, that for the n th line is given by $F_n = F_m/2^{n-m}$. For a given F , the I ratios of different lines may be very different. Similar results are to be expected for the $2p$ — np series of the Li I spectrum, with the difference that for lines characterised by the same term no. I_{\max} would be reached for F approx. half that for the corresponding line in the α -He spectrum. A. J. M.

Magnetic dipole transitions in the configurations $5p^5$, $5p^4$, $6p^5$ of xenon and radon. B. Edlen (*Physical Rev.*, 1944, [ii], 65, 248).—Three unidentified lines of Xe I and Xe II correspond with transitions between the series limits of these spectra. There is exact agreement with the ground-level separations of Xe II and Xe III as obtained from the extreme ultra-violet spectrum. The lines are due to magnetic dipole transitions, the theoretical probability of which is given. N. M. B.

Stark effect in dielectrics. A. A. Vorobiev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 770—771).—The absorption of light by crystals (rock-salt, Iceland spar, KI, NaBr, S, mica) placed in a strong electric field has been investigated. No displacement of the absorption limit in the ultra-violet (or for irradiated crystals, in the visible) was found, even though the field strength was only 10—20% < the breakdown strength. A. J. M.

Short-wave-length limit of the continuous X-ray spectrum and determinations of h/e . P. Ohlin (*Nature*, 1943, 152, 329—330).—The systematic error involved in X-ray determinations of h/e is investigated, using $\lambda\lambda$ 2498.42 and 2285.03. It is shown that a precise val. is obtained only if a sufficiently narrow, well-defined spectral band is used, and the voltage varied in small steps. E. R. R.

L-Series X-ray emission "outside the diagram." Application to a first experimental determination, by means of crystal spectrography, of the states of fundamental multiple ionisation of heavy atoms. (Mlle.) Y. Cauchois (*J. Phys. Radium*, 1944, [viii], 5, 1—11).—Recent results on a new family of satellites lead to a tentative estimation of the energies of atoms doubly ionised in profound layers. W. R. A.

L-Spectra and characteristic levels of hafnium (72) and weak L-emission of hafnium and tantalum. (Mlle.) I. Manescu (*Compt. rend.*, 1942, 215, 104—106).—The $\lambda\lambda$ and classification of lines are given. A. J. M.

Effect of chemical bond on X-ray absorption spectra. K. Main edge. I. B. Borovski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 764—769).—The structure of the K edge has been investigated for elements 22 (Ti) to 25 (Mn). The multiplicity of the K main edge is particularly considered. The transition between the beginning of the edge and the first kink (the so-called white line) corresponds to a transition to a comparatively weakly excited discrete 3d level. A white line is present not only for elements of higher valency, but also for Mn⁺⁺⁺, V⁺⁺⁺, and Co⁺⁺⁺. The behaviour of the short boundary of the edge depends essentially on the crystal structure of the compound used. The intensity of white lines in the long- λ part of the edge probably depends on the nature of the binding forces. When these are ionic the long- λ white lines will be particularly sharp. The Kunz rule (A., 1932, 669), that the difference of terms for the main edge of cations and metallic elements is \propto valency, needs to be supplemented. The val. of a term for a metal should be that corresponding to the middle of the interval between the beginning of the edge and the first kink. Further corrections are given for cations giving an edge with a white line, and for those without a white line. A. J. M.

Electron affinity of bromine and its decomposition on hot tungsten. P. M. Doty and J. E. Mayer (*J. Chem. Physics*, 1944, 12, 323—328).—The ratio of ions to electrons leaving a hot W surface in contact with Br vapour at low pressure corresponds to an electron affinity of 80.5 ± 0.4 kg.-cal. per mol. for Br. The decomp. of Br₂ is a first-order reaction between 1607° and 2276° K. and between 0.39 and 21.2 μ . pressure. The accommodation coeff. is unity. L. J. J.

Phase effects with coincidence proportional counters. C. L. Meaker and A. Roberts (*Rev. Sci. Instr.*, 1944, 15, 149—151).—The fraction of true coincidences measured can be a function of counter voltages and inter-counter absorber with certain amplifier characteristics and short time const. before the mixer stage. L. J. J.

Application of bursts of X-rays for the determination of the mobility of electrons in gases. P. Herrong (*Compt. rend.*, 1942, 215, 79—81).—An ionisation chamber with two plane, parallel metallic electrodes is arranged so that bursts of X-rays can be passed in, parallel to the electrodes. A uniform const. electric field is maintained between the electrodes. The bursts last for 10^{-6} sec., with a frequency of 50 per sec. All the ions formed are collected by the electrodes before the next burst follows. The current in the tube is amplified and passed on to a cathode-ray tube. The arrival of electrons at the anode is more rapid than discharge of positive ions, as is shown by a sudden discontinuity in the current-time curve, which, however, is usually rounded owing to diffusion. The mobility of the ions is calc. from the curve. For A at 340 mm., the mobility is 7650 cm. per sec. for a potential gradient of 1 v. per cm. This gives 91.6×10^{-3} cm. for the mean free path in A at 0° and 1 mm. pressure. The method is general and applies to ions of any mobility. A. J. M.

Photographic action of secondary electrons resulting from the action of X-rays on metals. J. J. Trillat (*Compt. rend.*, 1943, 216, 179—181).—In the use of an X-ray method of micro- or macro-radiography by reflexion (cf. A., 1943, I, 43) it is necessary to know the law of variation of photographic density as a function of at. no. of the irradiated element. This has been found for a no. of metals. The optimum range of X-ray energies is 150—200 kv. The photographic density increases rapidly with at. no. A. J. M.

Time scanning of impulse discharge spectrum. S. J. Bogdanov and K. S. Vulfovich (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 311—314).—A circuit for producing periodic discharges using a thyatron in series with a condenser and the discharge tube is described. Spectra of the impulse discharge in Kr at various c.d. show that lines belonging to the Kr II spark spectrum increase considerably in intensity with increase of c.d. The lines of the Kr I arc spectrum do not vary greatly in intensity with c.d. By using a rotating mirror, the variation of the spectrum during the impulse itself has been investigated. The behaviour of arc and spark lines can thus be examined. The emission of spark lines takes place during the first phase of the discharge, when the c.d. and ionisation are a max. The intensity of the arc lines attains a max. later in the discharge, when the spark lines are beginning to decrease. A. J. M.

Relative abundance of isotopes. L. B. Ponizovski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 104—108).—The max. no. of identical particles (neutrons or protons) added successively to a stable nucleus is 4. In a no. of cases the second or fourth proton is substituted by an aprotion (identical with the proton except in sign). It is shown that the max. no. of stable isotopes of one element is 10, formed by addition of 1, 2, 3, or 4 neutrons, 1 or 2 protons, and an aprotion on the main line or on branches. There is a periodicity of mass defect from the last particle added which is reflected in isotope abundance, in the main line of nuclear building. Nuclei on the branches of the main line are less abundant than the main nuclei of the same type, and nuclei due to addition of two protons or two neutrons at once are very rare. These rules are shown to hold true for 100 cases out of 116 where relative abundance is known. L. J. J.

Isotopic composition of snow. R. V. Teis and K. P. Florenski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 70—74).—Density measurements on H₂O from freshly fallen snow give negative deviations in the majority of cases. The mean deviation from ordinary H₂O is -2γ . Fractional electrolysis and interferometric and densimetric measurements show a deficit of D (-6 to -8.5γ) and an

excess of ^{18}O . Thawing is associated with accumulation of D and of ^{16}O in the solid phase. L. J. J.

Szilar isomerism effect. R. Daudel (*Compt. rend.*, 1943, 216, 46–48).—The recoil of atoms containing active nuclei at the moment of emission of electrons of internal conversion does not necessarily give rise to the breakdown of the mol. Although the energy required for rupture is $<$ that of the recoil, its probability is not 1. The probability of rupture of a Na_2SeO_3 mol. through emission of one of its electrons by internal conversion is considered. The coeff. of conversion is calc. The process of deactivation by emission of photons is very rare. The Szilar effect is due essentially to the ejection of electrons. A. J. M.

Disintegration schemes of radioactive substances. VII. ^{54}Mn and ^{58}Co . M. Deutsch and L. G. Elliott (*Physical Rev.*, 1944, [ii], 65, 211–215; cf. A., 1944, I, 76).—Investigations by magnetic lens spectrometer and coincidence techniques show that ^{54}Mn decays by orbital electron capture to an excited state of ^{54}Cr , followed by emission of a 0.835-Me.v. γ -ray. A large fraction of the captured electrons are K electrons. Few, if any, capture transitions lead directly to the ground state. ^{58}Co decays to a state of ^{58}Fe 0.805 Me.v. above the ground state, which in turn decays by the emission of a single γ -ray. About 90% of the disintegrations of ^{58}Co occur by K-electron capture, and in the remaining 10% positrons of max. energy 0.47 Me.v. are emitted. This ratio of the two modes of decay is consistent with the idea that the transition takes place with a change of angular momentum 1 or 0, whether the parity changes in the transition or not, if the tensor theory of β -decay is correct. The lowest known excited states of ^{54}Cr , ^{56}Fe , and ^{58}Fe have excitation energies differing by $<5\%$. The difference between the masses of the neutral atoms of ^{58}Co and ^{58}Fe should be $2.46 \pm 0.03 \times 10^{-3}$ a.m.u. N. M. B.

Isomerism induced in ^{115}In by electron impact. M. I. Korsunski, V. E. Ganenko, and S. I. Zipkin (*Compt. rend. Acad. Sci., U.R.S.S.*, 1941, 30, 403–404).—Monochromatised electrons (~ 1.6 Me.v.) bombarded two foils of In (0.06 cm.) separated by an Al plate (0.055 cm.). Thus the second In foil was exposed to γ -rays only and the difference in activities excited in the two foils was measured by a counter. Electron excitation occurred, and the effective cross-section for the electron effect is $\sim 2 \times 10^{-23}$ sq. cm. W. R. A.

Nuclear scattering cross-sections (σ) for chromium, silver, cadmium, and barium, with photoneutrons within the energy range 0.1–0.9 Me.v. T. A. Goloborodko (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 309–310).—The photoneutrons were obtained by irradiating Be and D with γ -rays from RaTh and Ra. The val. of σ varies with the energy of the scattered neutrons. Neutrons from RaTh- γ +D may be regarded as monochromatic, and of energy 0.2 Me.v. For neutrons from RaTh- γ +Be the energy is ~ 0.86 Me.v., but for Ra- γ +Be the neutron spectrum is not monochromatic, and the σ -vals. obtained with these neutrons represent mean vals. within the range 0.09–0.5 Me.v. A. J. M.

Cascade theory of cosmic showers. S. Belonki (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 608–612).—Arley's method (A., 1939, I, 116) for obtaining the energy spectrum of cosmic-ray showers is criticised, and a more general solution of the problem is offered. An equation is obtained from which the spectrum of electrons at any depth can be deduced. A. J. M.

Spectrum of the soft component [of cosmic radiation] in air at high energies. I. Pomerantschuk and A. Kirpitschev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 18–20).—The spectrum of decay electrons arising immediately from mesotron disintegration is used to calculate the spectrum of the soft component. The no. of particles of energy $>$ the crit. energy (e) is appreciable, e.g., 12–13% of the total soft charged component due to mesotron decay comprises particles with energy $>4e$, at sea level. L. J. J.

High-energy particles in Auger showers. A. Rogozinski (*Physical Rev.*, 1944, [ii], 65, 207–210).—Results are given of counter experiments at 10,618 ft. altitude on extensive atm. showers of 22 m. min. spread. A (master-group) method of investigation is described. High-energy electrons or photons, initiating a shower below a 10-cm. Pb screen, are accompanied, above the absorber, by a shower of high particle density located in the central part of, or close to, the core of the Auger shower. N. M. B.

Multiple production of penetrating secondary cosmic rays in lead. W. E. Hazen (*Physical Rev.*, 1944, [ii], 65, 249).—An explanation is given of the absence of indications of a "cascade" process in cloud-chamber photographs showing multiple production of penetrating particles by cosmic-ray neutrons and protons. N. M. B.

Method of shower anticoincidences for measuring the meson component of cosmic radiation. V. Sarabhai (*Physical Rev.*, 1944, [ii], 65, 250–251).—The use of the production of secondaries by the electronic component in cutting out the slow mesons is applied to bringing them into direct experimental observation. An arrangement of anticoincidence counters and Pb absorbers is described. Total intensity and meson intensity curves at two altitudes are given and discussed. N. M. B.

Is the "self-field" of the particle a physically observable quantity? M. Markov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 14–17).—A general theoretical discussion on the basis of existing theories. L. J. J.

Atomic wave functions for ground states of elements lithium to neon. W. E. Duncanson and C. A. Coulson (*Proc. Roy. Soc. Edin.*, 1943–1944, 62, 37–39).—Wave functions of the type proposed by Morse *et al.* (A., 1936, 133) are calc., and some errors in the latter are corr. H. J. W.

Generalised electrodynamics. II. Quantum. B. Podolsky and C. Kikuchi (*Physical Rev.*, 1944, [ii], 65, 228–235).—Mathematical. N. M. B.

New representation of types of nuclear forces. M. Bunge (*Physical Rev.*, 1944, [ii], 65, 249–250).—The physical meaning and the spatial symmetry properties of a system of nuclear particles can be described by a representation in which spin and isotopic spin are considered to be components of one quadrivalent variable. This representation does not, however, show whether a relativistic theory of the nucleon is possible without the introduction of four more states (antiproton and antineutron). N. M. B.

II.—MOLECULAR STRUCTURE.

Theory of hysteresis of rotational transformations. H. Hartmann (*Z. physikal. Chem.*, 1942, B, 52, 338–347).—The stability of the hysteresis loops observed for rotational transformations can be explained by Schäfer's theory (A., 1940, I, 11) only if the existence of forbidden transitions in the rotational term spectrum is assumed. A. J. M.

Application of new analysis of molecular spectra to interesting molecules. Simple explanation of some peculiarities of molecules. H. Deslandres (*Compt. rend.*, 1942, 215, 5–9).—A summary of rules obtained from a study of the infra-red spectra of hydrocarbons is given. A. J. M.

Excited states of the ethylene molecule. H. Hartmann (*Z. physikal. Chem.*, 1943, B, 53, 96–102).—Theoretical. Ground and first excited states of C_2H_4 are calc., and give the energy difference for the $\text{IS} \rightarrow \text{IIS}$ transition as 6.61 e.v., in fair agreement with Scheibe and Grieneisen's experimental val. of 6.48 e.v. (A., 1934, 583). R. C. M.

Experimental verification of the theory of the continuous spectra of H_2 and D_2 . A. S. Coolidge (*Physical Rev.*, 1944, [ii], 65, 236–246; cf. A., 1939, I, 165).—The spectra have been produced and studied under conditions permitting control of the excitation processes, the electron beam being subjected to definite accelerating potentials. Modifications to theoretical predictions show that no sharp separation of even the lowest vibrational level of the radiating electronic state can be expected at any accelerating potential. The form of functional relationship between the rate of excitation of a given level and the accelerating potential is found to be linear if the latter is somewhat $>$ the crit. excitation potential of the given level, and exponential if it is lower. Corrections to contact potentials are hence determined. At certain λ the observed radiation can come only from a single vibrational level; intensity-voltmeter readings give a curve in which the point where linear and exponential parts merge is taken as that at which the true accelerating potential equals the (known) crit. potential. When the true potential scale is thus established, there is good agreement between calc. and observed spectral energy distribution. N. M. B.

Ultra-violet spectrum of nitrogen molecule. (Mmc.) R. Herman and L. Herman (*Compt. rend.*, 1942, 215, 83–84).—The Kaplan bands of N_2 have been photographed. The lower levels of the Kaplan and the van der Ziel systems are not identical (cf. Kaplan, A., 1934, 823, 1279; van der Ziel, A., 1934, 575). A. J. M.

Spectrum of N_2 . R. E. Worley (*Physical Rev.*, 1944, [ii], 65, 249; cf. A., 1944, I, 27).—A note on the lettering of singlet states agreed on by Gaydon and the author, and a correction of an error in a table by the author (A., 1944, I, 27). An explanation of Hopfield's Rydberg series in emission is proposed. N. M. B.

Activation of nitrogen at liquid air temperature. S. S. Joshi and A. Purushotham (*Current Sci.*, 1944, 13, 155).—At liquid-air temp. the glow of N_2 suffers Rayleigh quenching at 15 mm. but not at >40 mm. With the discharge tube under liquid air Rayleigh quenching did not occur even at ~ 1 mm., but when the pressure was reduced to <0.1 mm. an afterglow persisting for 15–17 min. was observed, which is possibly due to adsorption of N_2 on the Pt and Al electrodes used. W. R. A.

Spectrum of deutoacetone in the vacuum ultra-violet. Comparison with the spectrum of acetone. (Miss) M. Lawson and A. B. F. Duncan (*J. Chem. Phys.*, 1944, 12, 329–335).—The absorption spectrum of $\text{CO}(\text{CD}_3)_2$ (I) has been photographed between 2000 and 1300 Å. with dispersion 4.14 Å. per mm. Some new ν for COMe_2 at $\sim 51,000$ cm^{-1} are recorded. ν are assigned to transitions for both compounds, and correlated with the normal state structures. The excited state of (I) shows no vibrational ν near 1200 cm^{-1} . This ν in COMe_2 cannot be ascribed to the C–O vibration. L. J. J.

Characteristic frequencies of some cyclic hydrocarbons. M. Parodi (*Compt. rend.*, 1942, 215, 13—15).—The fundamental ν of some modes of vibration of cyclo-pentane, -hexane, and -heptane are calc. on the assumption that the mols. are planar. There is satisfactory agreement with experiment, even in the case of cycloheptane, where the angle between consecutive valencies differs considerably from the tetrahedral angle. A. J. M.

Infra-red vibrations of certain organic crystals in the range of wave-lengths about 1 mm. E. Gross, A. Raskin, and V. Volkov (*Acta Physicochim. U.R.S.S.*, 1943, 18, 430—432).—The low-frequency scattering spectrum of crystals of NHPh_2 shows lines at frequencies 8, 39, 55, 80, and 133 cm^{-1} . The frequency of 8 cm^{-1} ($\lambda = 1.25$ mm.) is probably the lowest infra-red frequency observed heretofore with the aid of scattering spectra, and its use in several fields of investigations is discussed. C. R. H.

Analysis of infra-red absorption spectra of maleates and fumarates. (Mlle.) A. Delay, C. Duval, and J. Lecomte (*Compt. rend.*, 1943, 216, 40—42).—The infra-red absorption spectra of 18 maleates, 1 H maleate, 17 fumarates, and 1 H fumarate have been investigated. The fumarates have about half the no. of absorption bands of the maleates. The ion $\text{COO}\cdot\text{CH}\cdot\text{CH}\cdot\text{COO}$ has 24 distinct fundamental vibrations. The model with 4 masses, $(\text{COO})\cdot(\text{CH})_2\cdot(\text{CH})\cdot(\text{COO})$, has 6 fundamental vibrations, whilst that with 8 masses, $\text{COO}\cdot(\text{CH})_2\cdot(\text{CH})\cdot\text{COO}$, has 18. The ν corresponding to these vibrations are identified. Owing to the difference of ν which exists between the vibrations introduced by the presence of H atoms and those of the rest of the model, the model of the acids can be treated as one with 6 masses, $(\text{COO})\text{H}\text{C}\cdot\text{C}\cdot\text{C}(\text{COO})\text{H}$, and the vibrations are identified on this basis. A. J. M.

Absorption spectra of amido- and amino-complexes of bivalent platinum. A. V. Babaeva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 40, 61—65).—Absorption spectra (2200—6000 Å.) of 0.001—0.05M. aq. $\text{K}_2[\text{PtBr}_4]$, $\text{K}_2[\text{PtCl}_4]$, $\text{K}_2[\text{Pt}(\text{NCS})_4]$, $[\text{Pt}(\text{CS}(\text{NH}_2)_2)_2]\text{Cl}_2$, $\text{K}_2[\text{Pt}(\text{NO}_2)_4]\cdot 2\text{H}_2\text{O}$, $\text{K}_2[\text{Pt}(\text{C}_6\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$, and $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2\cdot \text{H}_2\text{O}$ have been examined and are discussed. The influence on the character of the spectrum of stepwise replacement of Cl by NO_2 in $\text{K}_2[\text{PtCl}_4]$ has been studied. W. R. A.

Absorption spectra of complex compounds. cis-trans-Isomerism of complex platinum compounds of the diamine series and light absorption. A. V. Babaeva (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 40, 148—151).—The absorption spectra (2200—6000 Å.) of 0.0001—0.01M. solutions of *cis*- and *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ (I), $[\text{Pt}(\text{NH}_3)_2\text{NO}_2\text{Cl}]$ (II), and $[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]$ (III) have been examined. (I) give three absorption bands. (II) and (III) show only one broad band, corresponding with the second band given by (I); in the *trans*-isomeride this band occurs at a higher λ than in the corresponding *cis*-isomeride. C. R. H.

Ultra-violet absorption spectra of freshly precipitated substances and colloidal solutions by reflexion. A. Berton (*Compt. rend.*, 1943, 216, 181—183; cf. A., 1938, I, 597).—An arrangement for obtaining the ultra-violet spectra of freshly pptd. substances by reflexion is described (see C., 1944, 200). The white $\text{Sn}(\text{OH})_2$ gel formed by pptn. of 10% SnCl_4 with aq. NH_3 gives a different spectrum from that of the substance which has been kept for 5 hr. in the mother-liquor. The change is due to dehydration. In the case of ZnS pptd. by H_2S from 10% $\text{Zn}(\text{OAc})_2$ there is a similar difference, also probably due to dehydration. The degree of dispersion of the freshly produced ppts. could also account for the change. However, the ultra-violet absorption spectra by reflexion of a sol and a gel of ZnS are the same as that of Zn blende. The spectrum of Ag sols shows the same min. of reflecting power at 3200 Å. as metallic Ag. The colloidal micelles are therefore composed of cryst. particles. A. J. M.

Absorption spectra of pyrrole-blue A and B. F. Fromm (*J. Amer. Chem. Soc.*, 1944, 66, 1227—1228).—The absorption spectra of pyrrole-blue A and B confirm the assumption that they possess different structures. W. R. A.

Molecular compounds of the quinyhydrone type in solution.—See A., 1944, II, 373.

Structure and properties of azo- β -naphthol dyes.—See A., 1944 II, 368.

New spectral method. Hertzian spectra of alcohol molecules. P. Girard and P. Abadie (*Compt. rend.*, 1942, 215, 84—86).—Investigation of the Hertzian spectra (λ 2.5 cm.—20 m.) of alcohols gives dispersion and absorption curves. The dispersion curves are directly related to the form of the mol., and the angle of the permanent moment with the plane or axis of symmetry can be determined. Alcohols with C_3 , C_8 , or C_{10} give curves of the same general type. The dispersion curve consists of a low plateau followed by a second region of dispersion, considerably higher. These have two different relaxation times, τ_1 , τ_2 , indicating two directions of oscillation of the mol. in the alternating field. Assuming that the polarisation is \propto (dielectric const.)², the angle which the permanent moment makes with the axis of symmetry of the mol. is 18° for both PrOH and $\text{C}_8\text{H}_{17}\cdot\text{OH}$. The ratio τ_1/τ_2 increases with the length of the C chain. It is ~ 3 times as great for $\text{C}_8\text{H}_{17}\cdot\text{OH}$ as for PrOH . Assuming the mols. to be ellipsoidal, the ratio of the axes can be calc. from τ_1/τ_2 , but the results do not agree with data obtained by X-ray diffraction, particularly for long-chain mols. A. J. M.

Hertzian spectra of benzyl alcohol and nitrobenzene. P. Girard and P. Abadie (*Compt. rend.*, 1943, 216, 44—46).—The forms of the mols. of $\text{CH}_2\text{Ph}\cdot\text{OH}$ (I) and of PhNO_2 (II) in the liquid state at ordinary temp. are deduced from their Hertzian spectra (λ 4 cm.—4 m.). In the case of (I) there are at least two regions of dispersion, and possibly three, ascribed to the following oscillations of the mol.: (1) oscillation of the C_6H_5 disc about a normal to the axis passing through the centre; (2) oscillation of the C_6H_5 disc about a perpendicular axis passing through the centre; (3) the probable third region indicates that the C_6H_5 ring is not quite circular owing to the presence of the side-chain. The components of the permanent moment in the ring plane are small. The mol. of (I) is therefore composed of an almost circular C_6H_5 ring, the permanent moment $^+\text{CH}_2\cdot\text{OH}$ making an angle of $\sim 70^\circ$ with the plane of the C_6H_5 . In the case of (II) there are two dispersion curves, one with a very small val. of the relaxation time, τ , corresponding to the rotation of the C_6H_5 disc about its axis, the other with a large val. of τ , corresponding to rotation about the normal to the axis. The τ of rotation of the C_6H_5 disc for (II) is 2.5 times that for (I), although the η of (I) is 3 times that of (II). In (II) the permanent moment (bisector of angle of O—N—O) and the two O atoms are all in the plane of the disc. A. J. M.

Fluorescence of polyatomic molecules. G. Kortüm and B. Finckh (*Z. physikal. Chem.*, 1942, B, 52, 263—283).—To investigate the connexion between fluorescence and chemical constitution, the mol. fluorescence spectrum of anthracene (I) in the solid state, in the form of vapour, and in solution in various solvents has been investigated, and compared with the corresponding absorption spectrum. The max. of the absorption spectrum are displaced ~ 1000 cm^{-1} towards longer λ in the series vapour, solution, crystal, but intensity and intensity distribution are approx. the same in all three states. The absorption and fluorescence spectra in dioxan solution are the mirror images of each other. The fluorescence bands in dioxan, MeOH , cyclohexane (II), and glycerol have the same position and intensity for solutions of the same concn. The polarity of the solvent and the concn. of the solution do not affect the position of the bands. The decrease in intensity of the mol. fluorescence with increasing concn. varies from solvent to solvent, and different bands are differently affected. The effect is least in dioxan. This is discussed in relation to various theories of polymerisation. The effect of temp. on the fluorescence is also examined. In the case of a solution in dioxan, the total intensity of the spectrum is reduced as temp. rises, but the positions of the bands and the relative intensity distribution are unchanged. Photometer curves for the fluorescence of (I) in (II) show that in very dil. solution outside the region of concn. extinction, the intensity of the fluorescence decreases very considerably with rise of temp. For medium concns. ($\sim 10^{-4}$ g.-mol. per l.) the decrease is very small, but at higher concns. the decrease is greater again. The fact that the temp. coeff. thus passes through a min. cannot be explained by increasing effectiveness of collisions of the second kind with rise of temp., but indicates that two effects occur. A. J. M.

Fluorescence of organic molecules. J. Weiss (*Nature*, 1943, 152, 176—178).—Quenching is explained on the conception of "trapping centres" by which electrons are prevented from returning to normal energy levels with fluorescence. E. R. R.

Effect of temperature on brightness of crystalline phosphors when excited by monochromatic radiation. M. Schön (*Naturwiss.*, 1943, 31, 169).—The effect of temp. ($< -190^\circ$) on the brightness of self-activated ZnS, Cu-activated ZnS—CdS, and self-activated ZnS—CdS phosphors has been investigated for monochromatic incident radiation of λ 4358, 4047, 3650, 3340, 3130, and 3025 Å. In the region of the fundamental lattice absorption, the brightness at low temp. increases with decreasing λ of the incident radiation, in agreement with the theory of Möglich *et al.* (A., 1942, I, 31). The luminescence of pure ZnS, which shows the greatest increase of brightness on cooling, decreases most rapidly on warming. For incident radiation of $\lambda >$ the fundamental lattice absorption, the brightness decreases with decreasing temp. A. J. M.

Broadening of the Rayleigh scattering lines depending on pressure. V. L. Ginzburg (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 399—402).—Theoretical. Existing theories are reviewed and a new one is developed. W. R. A.

Depolarisation of Raman lines of aqueous solutions of molybdates. (Mlle.) M. Théodoresco (*Compt. rend.*, 1943, 216, 56—58).—The Raman spectra of aq. solutions of Na and K molybdates have been investigated. There is only one polarised line, at 897 cm^{-1} for neutral Na molybdate, and at 894 cm^{-1} for neutral K molybdate. This is the very intense line due to symmetrical valency vibrations of hydrated MoO_4^{2-} . Study of the polarisation of the Raman lines has made it possible to find the components of the wide band which

accompanies the polarised line. There are only three lines characteristic of anhyd. MoO_4^{2-} . The H_2O mols. of the hydrated ion reduce the no. of elements of symmetry of the anhyd. ion.

$3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3 \cdot 4\text{H}_2\text{O}$ and $3\text{Na}_2\text{O} \cdot 7\text{MoO}_3 \cdot 22\text{H}_2\text{O}$ have only one polarised line at 938 cm^{-1} , corresponding to the only polarised line in the spectrum of metatungstic acid (950 cm^{-1}), and thus due to symmetrical valency vibrations of MoO_3 . A. J. M.

Depolarisation of Raman lines of simple and complex tungstates. (Mlle.) M. Théodoresco (*Compt. rend.*, 1943, 216, 117—118).—Neutral tungstates have only one polarised Raman line, characterised by its intensity. For Na tungstate it is at 931 cm^{-1} . The four components accompanying the polarised line, and together with it constituting the characteristic band, have frequencies 819, 833, 858, and 878 cm^{-1} . They all have different depolarisations. The so-called acid tungstates have a double polarised line constituting the most intense doublet of the characteristic band. The WO_3 group may have a pyramidal structure with W at the apex, symmetry group C_{3v} , or it could be planar, symmetry group D_{3h} . A. J. M.

Depolarisation of Raman lines. G. Glockler, J. F. Haskin, and (Miss) C. C. Patterson (*J. Chem. Physics*, 1944, 12, 349).—The use of a mica plate to rotate one of the components when using Polaroid in the measurement of depolarisation factors of Raman lines (Glockler and Baker, A., 1944, I, 3) is unnecessary if the two Polaroid films are positioned in front of the spectrograph so that their line of contact is at 45° to the vertical axis of the spectrograph. L. J. J.

Theory of intensities and polarisation in Raman spectra of halogen-substituted methanes. M. V. Volkenshtein and M. A. Eliashkevitch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1944, 43, 51—53).—The theory previously developed (A., 1943, I, 116) is applied to CCl_4 , CHCl_3 , CH_2Cl_2 , MeCl , MeBr , CH_2Br_2 , CHBr_3 , and CBr_4 . The original theory depends on the additivity of effects due to valency bonds, but this approximation is not always valid. The polarisability of a bond is not only a function of its length, but it also varies with the length of neighbouring bonds and with valency angle. However, the theory gives satisfactory agreement between observed and calc. vals. of intensity and polarisation, the agreement being better in the case of intensity. The calc. degree of depolarisation of deformational vibrations is $>$ observed vals. The polarisability (α) of the C—H bond is small, but the variation of α with bond-length (r) is considerable. $d\alpha/dr$ is the smaller the more ionic is the nature of the bond. A. J. M.

Raman effect and problems of constitution. XX. Dicyclohexadienes, a further contribution to the strain theory. K. W. F. Kohlrausch, R. Seka, and O. Trampusch (*Ber.*, 1942, 75, [B], 1385—1398).—Raman spectra of dicyclo-[2:2:2]-octane, 3:6-endoethylenhexahydrodimethylaniline, Et 2:5-endoethylenhexahydrobenzoate, Me₂ 3:6-endoethylenhexahydro-*o*-phthalate, tetrahydrodicyclohexadiene, dihydrodicyclohexadiene (mixture of isomerides), dicyclohexadiene, Me₂ 3:6-endoethylen- Δ^4 -tetrahydro-*o*-phthalate, Et 3:5-endoethylen- Δ^3 -tetrahydrobenzoate, 2:5-endoethylen- Δ^3 -tetrahydrobenzaldehyde, dicyclo-[2:2:2]-octene, dihydrodicyclohexadiene (possibly a mixture of isomerides), dihydrodicyclohexadiene (possibly mixed with tetrahydrodicyclohexadiene), and *trans*- Δ^2 -octahydronaphthalene are recorded and discussed. H. W.

Raman effect. CXXXVIII. Nitrogen compounds. XXV. Aromatic nitro-compounds. H. Witte (*Z. physikal. Chem.*, 1942, B, 52, 315—337).—The Raman spectra of PhNO_2 and $p\text{-C}_6\text{H}_4\text{F} \cdot \text{NO}_2$ have been reinvestigated and polarisation determinations have been carried out with PhNO_2 . The Raman spectra of cryst. *o*-, *m*-, and *p*- $\text{X} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ ($\text{X} = \text{OH}, \text{OMe}, \text{Cl}, \text{Br}, \text{CN}, \text{CO} \cdot \text{NH}_2, \text{CO}_2\text{H}, \text{CO}_2\text{Me}, \text{CHO}, \text{NO}_2$) (except *o*- $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$), and of three liquid nitroxylenes, have been investigated. The lines due to PhNO_2 and $p\text{-X} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ have been analysed, and the behaviour of the NO_2 valency frequency ω_6 and the valency frequencies $\omega(\text{C} \cdot \text{O})$ and $\omega(\text{C} \cdot \text{N})$ is considered. By *oo'*-dimethylation of PhNO_2 , ω_6 is raised, owing to steric hindrance, to a val. corresponding with that for $\text{CH}_2\text{Ph} \cdot \text{NO}_2$, in which lowering of ω_6 by mesomerism is not possible. An attempt is made to account for the change of ω_6 when PhNO_2 is mono-substituted, on the basis of the mesomeric effect, but a complete explanation is not achieved. A. J. M.

Raman effect. CXXXIX. Structure of diborane. J. Wagner (*Z. physikal. Chem.*, 1943, B, 53, 85—95).—Infra-red and Raman spectra of B_2H_6 are in better agreement with the ethylenic structure $\text{H}_2\text{BH}_2\text{BH}_2$ (symmetry group D_{2h}) than with the "ethane" formula, $\text{H}_3\text{B} \cdot \text{BH}_3$, suggested by Bauer (A., 1937, I, 397), Anderson and Burg (A., 1938, I, 600), and Stitt (A., 1942, I, 83). R. C. M.

Formation and structure of some organic molecular compounds. III. Dielectric polarisation of some solid crystalline molecular compounds. H. Kronberger and J. Weiss (*J.C.S.*, 1944, 464—469).—The mean dielectric consts. and mol. polarisations of the following mol. compounds and of the parent substances have been determined: anthracene (I)—picric acid; (I)—, benzidine—, 3:4-benz-pyrene—, chrysene—, coronene—, 20-methylcholanthrene—, phenanthrene—, $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ —, and pyrene- $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ —; quinydrone. The deviations from additivity of mol. polarisations in the case of

the compounds, which in some cases are considerable, are both positive and negative. The effects can be interpreted on the view that compound formation is accompanied by transfer of electrons. Coronene- $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$, which was cryst. from boiling C_6H_6 , decomposes below its m.p. Pyrene- $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$, m.p. 248° , was cryst. from C_6H_6 . C. R. H.

Measurement of the velocity of light in water. R. A. Houstoun (*Proc. Roy. Soc. Edin.*, 1943—1944, 62, 58—63).—The quartz ultrasonic diffraction grating (A., 1944, I, 146) was used, and the formula for the group velocity was verified with an accuracy of 0.1% for red, green, and blue light. H. J. W.

Havelock's formula and a new formula for the dispersion of electric and magnetic birefringence. R. Servant (*Compt. rend.*, 1943, 216, 177—178).—The formula previously proposed (*ibid.*, 1940, 211, 780) is compared with Havelock's formula. If it is supposed that the optical anisotropy is const. the theory of orientation agrees with Servant's formula but not with that of Havelock. A. J. M.

Light-scattering in solutions (and its applicability to optical analysis of solutions of polymers.) P. Debye (*J. Appl. Physics*, 1944, 15, 338—342).—A theoretical consideration of some of the conclusions derivable from measurement of light-scattering by turbid solutions; the possibility of mol. wt. determination by this principle is indicated. D. F. T.

Developments of valency theory. E. J. Bowen (*Chem. and Ind.*, 1944, 338—341).—A review dealing with the application of wave-mechanics to valency problems. The formation of a single link by the merging of electron clouds is described, and the wave-mechanical interpretation of the double bond is considered. Conjugation and the C_6H_6 formula are also discussed. Pauling's treatment is outlined. The association of liquids, and the nature of van der Waals forces, are considered. A. J. M.

Developments of valency theory. A. A. New (*Chem. and Ind.*, 1944, 367).—It is suggested that a dipole might be regarded as two atoms which have merged their electron clouds to give a pear-shaped form. This would give a method of representing a dipole on paper, the magnitude of the dipole moment being roughly represented by the sharpness of the pointed end. An error in a formula given by Bowen (preceding abstract) is reported. A. J. M.

Developments of valency theory. M. W. Travers (*Chem. and Ind.*, 1944, 367).—It is pointed out that "borohydrates" and B hydrides cannot be satisfactorily explained on the modern theory of valency (cf. Bowen, *supra*). A. J. M.

Co-ordination numbers of elements. P. Pfeiffer (*J. pr. Chem.*, 1943, [ii], 162, 279—306).—A review and classification. W. R. A.

Model for hydrogen bond (chain association of hydrogen fluoride). G. Briegleb (*Z. physikal. Chem.*, 1942, B, 52, 368).—Corrections to data used in a previous paper (A., 1942, I, 318) are reported. A. J. M.

Quantum mechanics of compounds. II. Bond system and stereochemistry of cumulenes. F. Seel (*Z. physikal. Chem.*, 1943, B, 53, 103—116).—Theoretical. Hund and Milliken's simplified theory (A., 1932, 10, 215, 562, 902, 1191) applied to allenes etc. gives structures in harmony with stereochemical behaviour. R. C. M.

Empirical correlation and method of calculation of barriers hindering internal rotation. J. G. Aston, S. Isserow, G. J. Szasz, and R. M. Kennedy (*J. Chem. Physics*, 1944, 12, 336—344).—The barriers hindering internal rotation of Me groups can be calc. by assuming that they are solely due to repulsion between H atoms according to the potential relation $V = 4.99 \times 10^6 r^{-5}$ between a H atom of a rotating group and a H atom of the remainder of the mol., assumed stationary and at a distance r . The vals. calc. are too low for Me_2O , Me_2S , and $\text{CHMe} \cdot \text{CH}_3$. Vals. are calc. for EtOH and PrOH and some *n*-paraffins, and entropy, heat capacity, and equilibrium const. vals. are calc. L. J. J.

Variation of thermal conductivity with pressure and the formation of double molecules in ethyl chloride. K. Schafer and O. R. F. Gazulla (*Z. physikal. Chem.*, 1942, B, 52, 299—314).—It is possible to determine the no. of double mols. in a gas by finding the variation of thermal conductivity with pressure. This variation is due to dissociation of the double mols., and it is possible to obtain from it the heat of dissociation and the equilibrium const. of the dissociation. The method is applied to EtCl . A method of obtaining the second virial coeff. is described; this makes it possible to separate the part due to swarm formation from that due to double mols. A. J. M.

Theory of the liquid state. I. Prigogine (*J. Phys. Radium*, 1944, [viii], 5, 16—22).—An approx. method is developed which permits the use of the Lennard-Jones and Devonshire model in the case where the van der Waals consts., but not the intermol. consts., are known. This theory is in good accord with experimental data. B.p. of ~ 40 substances have been calc. A quant. theory of the liquid state is given. The first five energy levels of H_2 for different

vals. of ν/ν^* have been computed. A val. of the sp. heat of liquid H_2 , in agreement with the experimental val., has also been calc.

W. R. A.

Surface tension and van der Waals' equation.—See A., 1944, I, 222.

Surface tensions of glasses.—See B., 1944, I, 334.

Rupture of water drops falling on liquid surfaces. B. N. Singh and S. P. Sinha (*Current Sci.*, 1944, 13, 157).—For drops of H_2O falling on an oil surface rupture takes place only when the drops fall from a height $>$ a crit. val. depending on the size of the drop and on the oil.

W. R. A.

Free energy of diffuse double layer. A. Frumkin (*J. Phys. Chem. Russ.*, 1943, 17, 310—312).—An explanation is offered for the difference between the energies of a condenser and an electric double layer.

J. J. B.

III.—CRYSTAL STRUCTURE.

X-Rays, crystals, and molecules. J. M. Robertson (*Proc. Roy. Phil. Soc. Glasgow*, 1943—1944, 58, 81—90).—A lecture.

Intensity measurements with focussing cameras of the Seemann-Bohlin type. G. Hagg and G. Regnstrom (*Arkiv Kemi, Min., Geol.*, 1944, 18, A, No. 5, 9 pp.).—A formula is derived for the calculation of X-ray reflexion intensities in powder photographs taken with Seemann-Bohlin type cameras, from photographic density data. Calc. and observed intensities agree within $\pm 20\%$ for NaCl powder samples with Cu K radiation.

L. J. J.

X-Ray topographs of diamond. G. N. Ramachandran (*Current Sci.*, 1944, 13, 156—157).—Description of a modification in technique of work already noted (A., 1944, I, 215).

W. R. A.

Abnormal diffusion of X-rays by diamond. A. Guinier (*Compt. rend.*, 1942, 215, 114—115).—A group of four very weak spots appears when a diamond crystal is turned a little from the position for reflexion from (111). One of these (diffuse) is due to thermal agitation. The other three are not affected by temp. and are sharp. For other positions of the crystal the spots are less intense and are less sharp. The explanation is discussed.

A. J. M.

Imperfect crystal. J. S. Anderson (*J. Proc. Roy. Soc. New South Wales*, 1943, 76, 345—358).—A lecture. The lattice imperfections displayed by heteropolar binary compounds and their influence on electrolytic conduction and on diffusion and reactions in the solid state are discussed in the light of recent advances in the knowledge of crystal structure.

C. R. H.

Lattice energy of ionic crystals. A. Kapustinski (*Acta Physicochim. U.R.S.S.*, 1943, 18, 370—377).—From the Born-Mayer quantum-mechanical equation for the energy of the lattice and the author's relation between structure coeffs. and ionic distances, the universal expression $U = 287.2\sum n \times v_1 v_2 / R \times (1 - 0.345/R)$ has been derived, where U is the lattice energy, v_1 and v_2 are valencies of cation and anion, R is the sum of the ionic radii (Goldschmidt's), and $\sum n$ is the no. of ions in the mol. The formula gives vals. within 2% of the observed vals. for numerous inorg. halides, oxides, sulphides, and selenides.

C. R. H.

Crystal chemistry of the Laves phases. G. B. Boki and E. E. Vainshtein (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 40, 232—233, and *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 241—247).—The intermetallic compounds which do not fit into the scope of the classical ideas of valency (Laves phases) have the formula AB_2 or $AB_2B'_2$. The structures of Laves phases are characterised by co-ordination nos. (12, 6), but each B atom has six B atoms as its closest neighbours; this accounts for the fact that similar structures are not observed in ionic compounds. These structures permit no variation in the ratio between the radii of the components; contact of uninomial spheres occurs with $R_A : R_B = 1.225$ and the $A-B$ distance $(a/8)\sqrt{11}$. The experimental vals. for $R_A : R_B$ lie between 1.11 and 1.33 (calc. vals. 1.09—1.34). Contrary to the views of Schulze, polarisation plays an important role, although mutual polarisation may sometimes be disguised by the influence of individual characters of the electronic structures of constituent atoms of the Laves phase. Elements participating in Laves phase formation are classed as (a) elements acting as A component only (Na, K, Ca, Ti, Ag, Pb, V, Cr, Mo, Re), (b) elements acting as B components only (Zn, Be, Co, Ni, Al), and (c) those capable of acting as either A or B (Mn, Fe, Cu, Au, Bi, Mg). Laves phases should not be regarded as an independent group of intermetallic compounds, and the term should be applied only to a definite type of crystal structure.

W. R. A.

X-Ray investigation of the structure of boron carbide. G. Shdanov and N. Sevastianov (*J. Phys. Chem. Russ.*, 1943, 17, 326—335).— B_4C forms a deformed NaCl lattice in which groups of 12 B and 3 C atoms play the part of Na and Cl'. The distances between various B atoms are 1.77, 1.78, and 1.80 Å, and between B and C 1.63 Å.

J. J. B.

Structure of nickel oxide. H. P. Rooksby (*Nature*, 1943, 152, 304).—X-Ray powder photographs taken on a 19 cm. diameter

camera show that some α -doublets are doubled or tripled. These observations are accounted for by a very slight distortion of the crystal from the face-centred cubic towards the rhombohedral; at 20° , $a_0 = 2.9459\text{Å}$, $\alpha = 60^\circ 4.2'$. The effect is common to NiO from many sources, but absent in FeO and CoO.

E. R. R.

Measurement of X-ray wave-lengths by the powder method: Cr $K\beta_1$ and Mn $K\beta_1$. H. Lipson and (Mrs.) L. E. R. Rogers (*Phil. Mag.*, 1944, [vii], 35, 544—549).—Using Cu $K\alpha$ and Co $K\alpha$ radiations as standards, the lattice parameter of powdered Si is found to be $5.41984 \pm 0.00005\text{Å}$ at 25° . From photographs taken with mixed radiations (Cu + Cr and Co + Cr) $\lambda = 2080.61 \pm 0.04\text{Å}$ for Cr $K\beta_1$. For Mn $K\beta_1$, different results were obtained according to whether the Mn was plated on Cu or Co in the target. For Mn on Cu, $\lambda = 1906.34 \pm 0.06\text{Å}$, and for Mn on Co, $\lambda = 1906.21 \pm 0.05\text{Å}$, the former val. being the one most likely to occur in practice.

H. J. W.

Unit cell and space-group of colemanite, $2CaO \cdot 3B_2O_3 \cdot 5H_2O$. V. A. Nikolski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 59).—Unit cell dimensions are: $a = 8.72 \pm 0.02$, $b = 11.29 \pm 0.02$, $c = 6.06 \pm 0.04$ Å; $a : b : c = 0.7728 : 1 : 0.5367$. Assuming $\rho = 2.42$ and $\beta = 110^\circ 09'$, the unit cell contains 2 mols. The most probable space-group is $C_{2h}^2 - P2_1/m$.

L. J. J.

X-Ray investigation of the structure of ammonium chloroiridate. G. B. Boki and P. I. Usikov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 782—784).—The crystals belong to the cubic system. Etched figures show that they belong to the hexaoctahedral class ($3L_4L_6^3L_9^3$). X-Ray analysis gives $a = 9.87$ Å; 4 mols. in unit cell; $\rho_{\text{calc.}}$ 3.06; space-group O_h^2 . The structure is similar to that of K_2PtCl_6 .

A. J. M.

Crystal structure of ammonium pentachlorozincate. H. P. Klug and L. Alexander (*J. Amer. Chem. Soc.*, 1944, 66, 1056—1064).—The crystal structure of $(NH_4)_2ZnCl_6$, determined from Laue and rotating and oscillating crystal photographs by the Patterson-Harker and Bragg-Fourier methods, is orthorhombic bipyramidal, $a = 8.74$, $b = 9.84$, $c = 12.61$ Å, space-group $D_{2h}^{18} - Pnma$, four $(NH_4)_2ZnCl_6$ mols. per unit cell. The positions of the atoms are fixed by 16 parameters. Zn atoms are surrounded by Cl atoms at 2.25 Å and one extra Cl not co-ordinated with Zn. These extra Cl atoms are surrounded by NH_4^+ ions at an average distance of 3.41 Å. One kind of NH_4^+ ion is surrounded by a trigonal prism of Cl atoms at an average distance of 3.44 Å, whilst the other NH_4 groups are surrounded by an irregular polygon of 8 Cl at an average distance of 3.32 Å. The Zn-Cl linkings in the $ZnCl_4$ tetrahedra are essentially covalent whilst all other bonds (N-H excepted) are essentially ionic. The structure consists of NH_4^+ , Zn^{++} , and Cl^- ions and the formula is $(NH_4)_2ZnCl_4 \cdot NH_4Cl$.

W. R. A.

X-Ray study of the copper-manganese binary alloy system.—See A., 1944, I, 276.

X-Ray examination of crystals of triphenylmethyl chloride and bromide. S. N. Wang and C. S. Lu (*J. Amer. Chem. Soc.*, 1944, 66, 1113—1114).—From X-ray examination of crystals of CPh_3Cl and CPh_3Br the hexagonal units of structure have $a_0 = 13.97 \pm 0.02$ and 13.86 ± 0.02 , $c_0 = 13.17 \pm 0.02$ and 13.36 ± 0.03 Å, six mols. per unit cell, space group $C_{3h} - H\bar{3}$ or $C_3^2 - H3$. The halogen atoms have been approx. located.

W. R. A.

Fine structure of polyamide fibres. K. Hess and H. Kiessig (*Naturwiss.*, 1943, 31, 171).—The condensation products of $NH_2 \cdot [CH_2]_n \cdot NH_2$ with adipic acid (polyamide HA) and with ϵ -aminohexanoic acid (polyamide ϵA) have been investigated. Very intense reflexions on the meridian were observed. They appear to be characteristic of this class of substance. The lattice-plane distance of the length period is ~ 74 Å. for HA and ϵA ; for fibres from poly- ω -hydroxydecanoic acid it is 79 Å., and for those from poly- ω -hydroxyundecanoic acid, 85.5 Å. For fibres from OH-acids the reflexions are weaker than from polyamide fibres. The identity periods, l_p , are 16.5 Å. for HA, and 16.8 Å. for ϵA , in good agreement with the calc. length of the fundamental group. If the stretched polyamide threads are heated the lattice plane distance is irreversibly increased to 95 Å. for HA and 120 Å. for ϵA , at 210° .

A. J. M.

Relation between structure of polyamides and that of silk fibroin. R. Brill (*Z. physikal. Chem.*, 1943, B, 53, 61—74).—The val. of 2.3 Å., calc. by Nowotny and Zahn (A., 1942, I, 354), from their experimental data, for the O-N distance (H-bond) in polypeptides is corr. by unpublished data of Brill, Hermann, and Peters to 2.85 Å. X-Ray examination of polyamides gives for the unit cell $a = 9.66$, $b = 8.32$, $c = 17.2$ Å., $\gamma = 65^\circ$ (a —distance between alternate zigzag chains). Comparison with data for silk fibroin (Kratky and Kurikama, A., 1931, 415) suggests that the structure of the latter is similar, with an extension of the b distance to accommodate side-chains, and lateral connexion of the zigzag chains in the ac plane by H-bonds between amide-N and carbonyl-O atoms, as in the polyamides and polypeptides.

R. C. M.

X-Ray studies of chain polymers. I. Fankuchen and H. Mark (*J. Appl. Physics*, 1944, 15, 364—370).—Consideration is given to the small-angle scattering of high polymers and to their X-ray micro-examination. Study of the former for oriented chain polymers

appears capable of indicating the existence of (quasi-)periodic heterogeneities perpendicular and (sometimes) parallel to the axis of stretch. The X-ray micro-technique permits the study of local heterogeneities, e.g., of weak spots in rayon yarns or the alteration in the structure of a polyamide fibre in the "necking down" area during drawing. D. F. T.

X-Ray structure of rubber and size and shape of rubber crystallites. S. D. Gehman and J. E. Field (*J. Appl. Physics*, 1944, 15, 371—379).—The cross-linked net-work of chain mols. in vulcanised rubber includes segments which locally are sufficiently free to form a crystal lattice on stretching. The crystallites so formed provide automatic reinforcement analogous in effect to that of a reinforcing filler. X-Ray investigation indicates that the size distribution of the crystallites is heterogeneous and includes small crystallites which broaden the base of the diffraction peaks and that a high degree of crystallinity is associated with small crystallite size. Increase in the proportion of combined S appears to limit crystallite growth but the widening of the diffraction spots in this case may alternatively be caused by lattice distortion. D. F. T.

Electron-microscopy of rubber latex and fibres.—See B., 1944, II, 296.

Lipins of tubercle bacilli. LXVI. Structure of tuberculostearic acid.—See A., 1944, II, 319.

Electronographic investigation of the structure of lead iodide. Z. Pinsker, L. Tatarinova, and V. Novikova (*Acta Physicochim. U.R.S.S.*, 1943, 18, 378—386).—The investigation has established the existence of two modifications. PbI_2 obtained by crystallisation from aq. solutions belongs to the space-group D_{3d}^2 with one mol. per unit cell, and cell dimensions a 4.54, c 6.90 Å. PbI_2 obtained by sublimation belongs to the space-group with 3 mols. per unit cell and a 4.54, c 20.7 Å. At. parameters are given. C. R. H.

Electron-microscopic study of dextran molecules. B. Ingelman and K. Siegbahn (*Arkiv Kemi, Min., Geol.*, 1944, 18, B, No. 1, 6 pp.).—A dil. dextran solution dried on zapon lac foil shows a branched thread-like structure with magnification 65,000 diameters. The threads have a min. thickness 30—100 Å., with swellings at intervals of ~800 Å. The observed thickness is of the order expected for the polysaccharide chains. L. J. J.

Magnetisation of polycrystalline iron and iron-silicon alloys. G. C. Richer (*Iron and Steel Inst.*, Sept., 1944, *Advance copy*, 50 pp.).—A survey has been made of the competency of the domain theory of ferromagnetism to account for the observed characteristics of such material. This theory is described and its relations to the virgin magnetisation curve of single crystals, the magnetisation curve of polycryst. aggregates, and the cyclic magnetisation and the hysteresis effect are discussed. It is concluded that the basic theory can provide reliable guidance for industrial effort, though unexplained discrepancies between theory and observations exist. A new method has been evolved for analysis of the technical magnetisation curve. T. D. F.

Hysteresis of polycrystalline ferromagnetics in weak magnetic fields. E. Kondorski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 603—607).—In extension of previous work (A., 1940, I, 200) an approx. theory of hysteresis of polycryst. ferromagnetic substances is developed, account being taken of the magnetic interaction between the separate parts. Equations obtained for hysteresis work agree with those of Rayleigh. A. J. M.

Magnetostriction of polycrystals. K. V. Vladimirov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 10—13).—It is shown that the microscopical magnetostriction of polycrystals can be expressed in terms of the free strains as the vol. average with a weighting factor representing the stress at a given point of the body when extended by the forces applied at the external surface. As an example the longitudinal magnetostriction of polycryst. Fe between its demagnetised state and saturation is calc. L. J. J.

Discharges in rock-salt crystals. A. A. Vorobiev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 772—774).—The spreading of an electric discharge through crystals owing to the presence of mechanical strains has been investigated. Spreading of the discharge does not occur within parts of the crystal subject to pressures approaching those causing fracture. The discharge proceeds along the boundary between the strained and unstrained parts in the direction of the greatest gradient of strain. Discharges in crystals with regions of different concn. of free electrons were also studied. The length of the discharge in the part of the crystal which has an increased concn. of free electrons is about twice as great as that in the original crystal. The path of the discharge is more branched, and the discharge is stronger. The breaking up of the crystal along the path of the discharge is also more marked. When the point electrode is positively charged the path of the discharge follows the crystallographic axes, and is unaffected by an applied electric field. When the point is negative, the direction of the discharge is less definite, and is more easily affected by the application of an electric field. A. J. M.

Form of the first Brillouin zone in the case of hexagonal structure of nickel arsenide type. E. S. Makarov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 40, 191—193).—The low or negative temp. coeff. of electrical conductivity in Fe-Ni-Sb alloys with Ni arsenide structure implies nearly complete filling up of the Brillouin zone, which should include ~2.5 electronic states per atom. Data from powder photographs show that the shape of the Brillouin zone is a combination of 3 types of plane, (022—112), (200—130), and (002), with vol. in the K -space $(32a^2 - 2c^2)/3\sqrt{(3a^2 - c^2)}/6a^2$ states per atom. Vals. for Fe-Sb (47.1 at.-% Sb), Co-Sb (48.2 at.-% Sb), and Ni-Sb (49.46 at.-% Sb) are 2.402, 2.372, and 2.386 states per atom. Overlapping into the second zone occurs across the (002) plane, and accounts for electrical properties and metallic character. L. J. J.

Inversion of direction of dispersion of anisotropy in some opaque orthorhombic crystals. L. Capdecombe (*Compt. rend.*, 1942, 215, 88—90).—The anisotropy of reflexion of a uniaxial section is the ratio of the two principal reflecting powers. There is an inversion in the direction of the dispersion in the case of some orthorhombic crystals, including enargite, manganite, and stibine. A. J. M.

Debye's transverse heat waves and the scattering of light in crystals. E. Gross (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 757—759).—The existence of six components of the Rayleigh line in crystals (cf. A., 1938, I, 175) is discussed. Their origin may be explained by supposing that the two displaced components are due to Debye's longitudinal heat waves, and the four additional components are due to light scattered from two transverse heat waves of the acoustic spectrum of the crystal. This view is confirmed by the determination of the shifts of λ in the displaced components in quartz. The velocities of propagation of the longitudinal and transverse heat waves can be obtained from these displacements, the results being 6400 m. per sec. for the longitudinal, and 3500 and 2800 m. per sec. for the two transverse, waves. These vals. are in good agreement with those obtained from the known velocities of propagation of longitudinal and transverse waves along the direction of the crystal which would be taken by the elastic waves scattering the light, calc. from the torsion moduli. The results are also in agreement with the amount of light scattered by crystals, and are confirmed by the work of Michailov on the diffraction of light at high-frequency transverse elastic waves in cubic crystals (see following abstract). A. J. M.

Diffraction of light from high-frequency transverse elastic waves in cubic crystals. I. G. Michailov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 760—763).—The propagation of ultrasonic waves through crystals is accompanied by the formation of longitudinal and transverse waves. Like the longitudinal waves, the transverse waves can also act as a diffraction grating. This effect with transverse waves has been investigated for NaCl and KCl crystals. The torsion moduli of NaCl and KCl calc. from the diffraction agree with the vals. obtained by Voigt (1888) by the static method. Under different conditions of excitation it is possible to observe the diffraction of light from the first and second transverse waves individually. The directions of the vibrations of the two waves are at right angles to each other. In order to obtain diffraction with both waves simultaneously the crystal must be oriented in such a way that the directions of vibration of the waves make an angle of 45° with the direction of the light. The diffraction phenomena could be observed with comparatively low ultrasonic-wave energies. A. J. M.

Morphology of liquids. IV. Stable, individual liquid crystal structures. G. Weygand (*Z. physikal. Chem.*, 1943, B, 53, 75—84; cf. A., 1944, II, 179).—In p -C₆H₄·O·C₆H₄·CH·N·C₆H₄Pr- p the following liquid crystal transitions are observed: liquid (85°) \rightleftharpoons nematic I (83°) \rightleftharpoons smectic I (70°) \rightleftharpoons smectic II (54°) \rightleftharpoons smectic III \rightarrow solid (m.p. 54.5°). The smectic III phase is a supercooled liquid. Doubly refracting structures, for which the name "crystalloid" is proposed, separate from a 7% alcoholic solution on cooling. The observations are discussed. R. C. M.

IV.—PHYSICAL PROPERTIES OF SUBSTANCES.

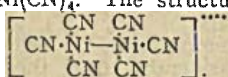
Mol. wt. in high polymers.—See A., 1944, I, 201, 202.

Ferromagnetism of thin layers of nickel. A. Colombani (*Compt. rend.*, 1943, 216, 115—117).—An oscillograph method (cf. A., 1940, I, 176) has been used to study the ferromagnetism of thin layers of Ni. Unannealed layers have a very weak ferromagnetism, with very slight hysteresis. X-Ray analysis indicates that these layers are composed of groups of atoms. Layers of thickness <220 μ ., after being heated to 410° , show little change in magnetic properties or in X-ray structure. Between 220 and 360 μ ., the hexagonal structure appears, but there is still only weak ferromagnetism. For thickness >360 μ ., a very strong ferromagnetism is observed, and the structure becomes face-centred cubic. The magnetic properties are related to the electrical conductivities of the layers. A. J. M.

Magnetic studies of chromium oxide catalysts. J. Turkevich (*J. Chem. Physics*, 1944, 12, 345—346).—No difference in magnetic susceptibility between active Cr oxide gel and "glowed" inactive

Cr oxide is found from -183° to 444° . Activated adsorption of H causes no magnetic change. The active oxide, obtained by interaction of $\text{Cr}(\text{NO}_3)_3$ with NH_3 , is intermediate in composition between Cr_2O_3 and CrO_3 . L. J. J.

Magnetic behaviour of potassium cyanonickelate. D. P. Mellor and D. P. Craig (*J. Proc. Roy. Soc. New South Wales*, 1943, **76**, 281—282).—A new examination of $\text{K}_2\text{Ni}(\text{CN})_6$ shows that it is diamagnetic with a susceptibility approx. the same as that of $\text{K}_2\text{Ni}(\text{CN})_4$. The structure of $\text{K}_2\text{Ni}(\text{CN})_6$ probably involves the ion



C. R. H.

Magnetic properties of porous substances. C. Courty (*Compt. rend.*, 1942, **215**, 18—20).—The variation of susceptibility of porcelain and activated C in passing gradually from an atm. of dry air to one saturated with H_2O vapour, and then when completely immersed in H_2O , has been investigated. The additive rule applies to porcelain and H_2O . With coconut C in bulk the rule does not apply, but when the substance is powdered it holds well. Non-activated C is diamagnetic, but after activation with H_2O or CO_2 it is paramagnetic. It is shown that the physical consts. of air adsorbed by C are different from those of free air, and that there is a difference between the nature of the porosity of porcelain and that of C.

A. J. M.

Diamagnetic anisotropy of crystalline liquids. V. Zvetkov and A. Sosnovski (*Acta Physicochim. U.R.S.S.*, 1943, **18**, 358—369).—Measurements of the diamagnetic anisotropy of *p*-methoxycinnamic acid, *p*-azoxy-anisole and -phenetole, di-*p*-acetoxybenzylideneazaine, anisylidene-azine and -*p*-aminoazobenzene, and dibenzylidene- and dianisylidene-benzidine are recorded. The data support the view that magnetic anisotropy is essentially determined by the no. of C_6H_5 rings in the mol., observed discrepancies being due possibly to anisotropy of non-aromatic groups. C. R. H.

Propagation of sinusoidal thermal waves in a heterogeneous medium. M. Parodi (*J. Phys. Radium*, 1944, [viii], **5**, 23—24).—Mathematical. W. R. A.

Optical properties of very thin layers of chromium obtained by thermal projection. M. Perrot (*Compt. rend.*, 1943, **216**, 38—40).—Reflexion and transmission coeffs. of thin films of Cr obtained by cathodic sputtering on to glass surfaces indicate that the film is an oxide layer. By thermal projection in vac., films of pure Cr were obtained, and the coeffs. of reflexion from air-metal and glass-metal interfaces, and the coeff. of transmission, were obtained. The min. coeff. of reflexion from glass-metal occurs for a thickness of metal varying with λ . The coeff. of reflexion for air-metal shows a max. followed by a min. as thickness increases, at all λ . The vals. obtained are quite different from those for the oxide film.

A. J. M.

Variations of phase on normal reflexion from very thin layers of chromium obtained by thermal vaporisation. M. Perrot (*Compt. rend.*, 1943, **216**, 150—152).—There is a change of phase on reflexion from very thin layers of Cr deposited on quartz. In addition to the variation of phase difference with thickness of the film, there is a jump in phase of 2π for films of thickness 15—20 μ . A. J. M.

Optical constants of tungsten and antimony determined by reflected polarised light. L. M. Chatterjee and K. N. Prasad (*Current Sci.*, 1944, **13**, 177—178).—Optical consts. of Sb and W in the range 4600—6600 Å. have been measured. By using specimens hand-polished to different extents, the effect of polishing has been investigated. W. R. A.

Small-angle interference of myosin.—See A., 1944, III, 746.

Specific heats of hydrocarbon gases.—See B., 1944, I, 356.

Heat capacity of carbon tetrachloride from 15° to 300°K . Heats of transition and fusion. Entropy from thermal measurements compared with the entropy from molecular data. J. F. G. Hicks, J. G. Hooley, and C. C. Stephenson (*J. Amer. Chem. Soc.*, 1944, **66**, 1064—1067).— C_p vals. have been determined calorimetrically for CCl_4 from 17.09° to 298.49°K . The m.p. is $250.3 \pm 0.1^{\circ}\text{K}$. and there is a transition point at $225.35 \pm 0.03^{\circ}\text{K}$. Heats of transition and fusion are 1095 ± 3 and 601 ± 2 g.-cal. per mol. Vals. of entropy from calorimetric data are: liquid 51.25 ± 0.15 ; gas 73.7 ± 0.3 g.-cal. per degree per mol. at 298.19°K . The vals. are compared with those derived from mol. data (74.0 — 74.3 g.-cal. per degree per mol.). W. R. A.

Heat capacity and entropy, heats of fusion and vaporisation, and vapour pressure of trimethylamine. Entropy from spectroscopic and molecular data. J. G. Aston, M. L. Sagenkahn, G. J. Szasz, G. W. Moessen, and H. F. Zuhr (*J. Amer. Chem. Soc.*, 1944, **66**, 1171—1177).— C_p has been measured calorimetrically from 11.88° to 275.90°K . for NMe_3 (m.p. $156.08 \pm 0.06^{\circ}\text{K}$; b.p. $276.03 \pm 0.05^{\circ}\text{K}$). The v.p. determined from 190°K . to the b.p. can be represented by $\log_{10} P (\text{mm.}) = -2141.7743/T - 11.400327 \log T + 0.006349001T + 36.715267$. The heats of fusion and vaporisation (at b.p. and at 250.00°K , 250.01 mm.) are 1564.0 ± 1.0 , 5482.4 ± 7 , and 5822.6 ± 7 g.-cal. per mol. Vals. of vapour density fit the equation

$\rho/P = 0.000079051P + 0.00241364$. The following entropy (S) vals. were derived from calorimetric data: liquid at m.p. 30.857 ± 0.09 ; liquid at normal b.p. 47.28 ± 0.14 ; superheated liquid at 298.16°K . 49.82 ; ideal gas at 200.00° , 250.00° , and the b.p. 61.60 ± 0.14 , 65.39 ± 0.16 , 67.31 ± 0.19 g.-cal. per degree per mol. An assignment of the Raman spectrum has been made and the vals. of S from spectroscopic data are: 200°K , 61.60 ; 250°K , 65.39 ; b.p., 67.31 g.-cal. per degree per mol. W. R. A.

Apparent second-order transition point of polystyrene. T. Alfrey, G. Goldfinger, and H. Mark (*J. Appl. Physics*, 1943, **14**, 700—705).—At $>80^{\circ}$ the sp. vol. (dV/dT) of polystyrene (I) is 0.00043 , whilst at $<40^{\circ}$ it depends on the past thermal history and is 0.00024 . When (I) is cooled at a const. rate it contracts to the higher expansion coeff. until some crit. region of temp. and then contracts to the smaller coeff., but the position of the crit. temp. depends on the rate of cooling, being higher at faster rates. Between 40° and 80° complex time effects are observed. Results accord with a "second-order transition point" of (I) as the temp. at which rate of vol. change becomes comparable with the experimental time scale.

W. R. A.

Specific and latent heats of fusion of vegetable fats and oils.—See B., 1944, II, 287.

Thermal expansion of concrete aggregate materials.—See B., 1944, I, 368.

Van der Waals' equation of state and the compressibility of molecules. D. B. Macleod (*Trans. Faraday Soc.*, 1944, **40**, 439—447; cf. A., 1937, I, 355).—If van der Waals' equation is written $P(v - b') - RT$, where $P = p + a/v^2$ and $b' = b_0(1 - BP + CP^2)$, satisfactory consts. can be found for a no. of typical org. fluids when $b'_0 \sim v_c/2$. Substituting this val. of b'_0 in the equation for the crit. point a can be calc. directly from crit. data, and $(P + a/v^2)$ can thus be obtained from experimental vals. of p and the corresponding mol. vols. If the consts. B and C are now used to calculate b' , the resulting vals. of $RT/(v - b')$ are found to agree closely, for CO_2 , at the crit. temp., with those of $(p + a/v^2)$ obtained as described. Hence b' can be expressed very accurately as a function of P when $b'_0 = v_c/2$, but not if $b'_0 = v_c/3$ as required by the simple form of the equation. Corresponding vals. of P and $RT/(v - b')$ are tabulated for CCl_4 , $n\text{-C}_6\text{H}_{14}$, and C_6H_6 , for both liquid and vapour phases, and good agreement is shown over a wide range of temp. Vals. of the consts. a , b_0 , B , and C are given for these substances and for CO_2 and Et_2O . It is claimed that b_0 represents the mol. vol. of the mols. in the extreme gaseous condition; the val. of b' undergoes changes of 30—40% in passing from the vaporous to the liquid state. These changes may represent an actual compressibility of the mols. For elementary substances and those for which the val. of $RT/p_c v_c$ lies between the theoretical 2.67 and the more usual 3.8, $b'_0 = v_c/2$ no longer gives satisfactory results, and a suitable val. must be found by trial. Thus for H_2 , $b'_0 = 0.36v_c$. F. L. U.

Thermal and electrical conductivity of graphite and carbon at low temperatures. R. A. Buerschaper (*J. Appl. Physics*, 1944, **15**, 452—454).—The transverse and longitudinal thermal conductivities of graphite are measured in the range 191 — 100°K ; they show an increase with decrease in temp., the latter being about half the val. of the former. The electrical conductivities show a decrease with decreasing temp., the former having again the larger val. For C both thermal and electrical conductivities show a decrease with decreasing temp. J. H. BA.

Viscosity of hydrogen fluoride. J. H. Simons and R. D. Dresdner (*J. Amer. Chem. Soc.*, 1944, **66**, 1070—1072).—Details are given of a viscometer suitable for determining η of HF between -70° and 10° (see C., 1944, 204). η has low vals. (approx. the same as Et_2O in the same temp. range) which are raised greatly by small amounts of EtOH . W. R. A.

Applicability of the principle of similitude of H. Kramerslingh Onnes to prediction of the magnitude of viscosity. M. Trautz (*J. pr. Chem.*, 1943, [ii], **162**, 218—223).—Mathematical. W. R. A.

Reynolds number and liquid helium II. D. V. Gogate (*Current Sci.*, 1944, **13**, 177).—Since the flow of liquid He II is independent of pressure, the Reynolds no. should be const. W. R. A.

Viscosity of mercury under the action of a magnetic field. G. Destriau and G. Massieu (*Compt. rend.*, 1942, **215**, 64—65).—In a method in which the effect of Foucault currents was reduced to a min., η of Hg in very fine tubes was found to increase with increasing magnetic field strength, up to a max. at 13,500 gauss. Under these conditions η is 7% > normal. A. J. M.

V.—SOLUTIONS, DISPERSIONS, AND MIXTURES.

Thermal diffusion of gases. Method of Clusius and Dickel. A. Fournier (*J. Phys. Radium*, 1944, [viii], **5**, 11—16; cf. A., 1938, I, 539).—Theoretical. An elementary theory of the thermal diffusion of gases, which takes into account only the mass of the mols., is

given. The influences of factors other than mol. mass predominate in thermal diffusion of mixtures of gases of equal mol. mass.

W. R. A.

Thermal diffusion in liquids. H. Carr (*J. Chem. Physics*, 1944, **12**, 349).—A thermal diffusion tube $1.59 \times 0.057 \times 100$ cm., with temp. difference 49° between upper and lower sides, shows concn. differences increasing with time between samples from top and bottom. ZnSO_4 (0.6M) showed concns. differing by a factor of 17.1 after 12 hr. when the tube was inclined at 45° . The max. effect after 2 hr. was given with 45° inclination and concn. 0.6M.

L. J. J.

Viscosity of aqueous solutions of calcium chloride at 35° . T. Patnaik and B. Prasad (*J. Indian Chem. Soc.*, 1944, **21**, 125—126).— η and d data for 0.001—0.05M- CaCl_2 are recorded. The η data obey the Jones-Dole equation.

C. R. H.

Viscosity and vapour pressure of dilute solutions. II. Relation between viscosity and vapour pressure. H. G. de Carvalho (*Anais Assoc. Quim. Brasil*, 1944, **3**, 88—94).—It is deduced that the relationship between viscosity (η) and v.p. (p) is $p\eta^a = k$, where a is a const. for each substance and varies with temp. This relation combined with Raoult's law gives $\eta = \eta_0(1 + n/N)^{1/a}$ (η_0 applies to the solvent, n and N are g.-mols. of solute and solvent), which is applicable to glycerol up to 7% concn. Osmotic pressure is thence $(aRT \log \eta/\eta_0)/V_0$ and mol. wt. of the solute is $M_0 w \eta_0^a / W(\eta^a - \eta_0^a)$, where V_0 is the partial mol. vol. of solvent in the solution, and W is the no. of g. of solvent of mol. wt. M_0 containing w g. of solute.

F. R. G.

Molar friction coefficients in solutions of associated and solvated substances with special reference to diffusion theory. O. Lamm (*Arkiv Kemi, Min., Geol.*, 1944, **18**, A, No. 10, 11 pp.).—The friction coeffs. (mean friction per g.-mol.) are considered in the case of a two-component system where one component diffuses into more dil. solution. Under ideal conditions the mean friction coeff. in the case of diffusion agrees with that calc. from sedimentation velocity. There is also agreement between diffusion and ionic mobility, as required by the Nernst theory of diffusion.

A. J. M.

Theory of diffusion with special reference to characteristic diffusion. O. Lamm (*Arkiv Kemi, Min., Geol.*, 1944, **18**, B, No. 5, 8 pp.).—The characteristic diffusion of two- and three-component systems should be independent of the proportions of the mixture, although this is not directly established by the author's theory. Elementary statistical considerations are now shown to lead to the expected results.

A. J. M.

Charge effect in sedimentation and diffusion determinations and determination of mol. wt. of high-molecular metaphosphates. O. Lamm (*Arkiv Kemi, Min., Geol.*, 1944, **18**, A, No. 8, 7 pp.).—The charge on the high-mol. metaphosphate ion when completely dissociated is very high, and can give rise to anomalies in vals. of the mol. wt. calc. from sedimentation and diffusion observations. The conductivities of 0.4M- NaCNS (I), (I) + 0.547% of K metaphosphate (corresponding to 0.0463M- KPO_3), and (I) + 0.0463M- NaCNS were determined. The increase in conductivity for the KPO_3 was 0.12×10^{-2} , whilst that for the equiv. addition of NaCNS was 0.25×10^{-2} . The KPO_3 has mol. wt. $\sim 160,000$ and is 0.33 dissociated. The effect of charge is considered, and the correcting factor is calc. Although it cannot be neglected it does not greatly affect the calc. val. of the mol. wt.

A. J. M.

Theory of diffusion of ternary solutions. O. Lamm (*Arkiv Kemi, Min., Geol.*, 1944, **18**, A, No. 2, 10 pp.).—Complete differential equations for diffusion in a three-component system are derived.

L. J. J.

Light absorption of nickel acetate and nickel perchlorate. K. Veeraiiah and M. Qureshi (*J. Indian Chem. Soc.*, 1944, **21**, 127—130).— $\text{Ni}(\text{OAc})_2$ solutions show continuous absorption in the violet region with a max. in the red at $\sim 715 \mu\mu$. Dilution increases the mol. extinction coeff. especially in the region of max. absorption, although the position of the max. is unchanged. $\text{Ni}(\text{ClO}_4)_2$ solutions show similar characteristics but the max. in the red shifts to lower wave lengths on dilution.

C. R. H.

Interferometric studies of light scattering in binary liquid mixtures. II. K. S. Bai (*Proc. Indian Acad. Sci.*, 1944, **20**, A, 18—23).—The scattering of light by 7 PhOH- H_2O mixtures has been examined spectro-interferometrically. For mixtures containing 15, 28, 34, and 60 wt.-% PhOH Brillouin components are absent, indicating the presence of mol. clusters of size comparable with the λ of light, whilst in mixtures containing 10, 70, and 80 wt.-% PhOH Brillouin components are present, weakly at 80° and more pronounced at higher temp., indicating the breaking up of large clusters to smaller groups. The tendency to form mol. clusters was greatest at the crit. composition, in agreement with other optical data.

W. R. A.

Dielectric polarisation of solid organic molecular compounds.—See A., 1944, I, 267.

Analysis data for ternary system acetone-benzene-water. E. Honold and H. Wakeham (*Ind. Eng. Chem. [Anal.]*, 1944, **16**, 499—501).— n and d of mixtures in the homogeneous region of the system

have been determined at 25° . Lines of equal n and of equal d are plotted on a triangular diagram against composition of the mixture. The graph enables the composition of a homogeneous mixture to be read off if the n and d at 25° are known. Cloud point compositions at 25° may also be derived.

F. Hu.

Supersaturation limits of solutions. II. R. Gopal, III. R. Gopal and A. C. Chatterji (*J. Indian Chem. Soc.*, 1944, **21**, 103—108, 145—147).—II. The investigation reported previously (cf. A., 1943, I, 302) has been extended to K_2SO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, K_2CrO_4 , and HgCl_2 . The vals. of $\lambda(T_s - T)$, where λ = heat of dissolution, T_s = saturation temp., and T = temp. of first spontaneous crystallisation, vary considerably from the val. 80,000 g.-cal. found for univalent K and Na salts. On the other hand, $\lambda(T_s - T)/\sigma V_m$, where σ = sp. surface energy and V_m = mol. vol., is reasonably const. (~ 13.0), i.e., for substances with V_m vals. approx. equal, the limit of supersaturation $(T_s - T) \propto 1/\lambda$. From the relation $\lambda(T_s - T)/\sigma V_m = 13.0$ the radius (r) of the stable crystal nucleus has been calc. Its val. increases from 1.0×10^{-6} to 1.13×10^{-6} cm. as T_s increases from 10° to 40° . If T_s for a given solute is kept const., $r(T_s - T) = \text{const.}$

III. From a consideration of the Jones-Partington equation it has been shown that vals. of λ at ordinary temp. can be substituted for vals. at abs. zero (λ_0) in the derived equation $\lambda_0(T_s - T) = 2M\sigma T_s/\rho r$ where M and ρ have their usual significance.

C. R. H.

Solid solutions of calcium and strontium orthosilicates. N. A. Toropov and P. F. Kononov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **40**, 155—157).— d_4^{20} and n data for solid solutions in the system Ca_2SiO_5 - Sr_2SiO_5 are recorded. The solid solutions exist in a continuous series.

C. R. H.

Polymer chemistry of silicates, borates, and phosphates. S. B. Hendricks (*J. Washington Acad. Sci.*, 1944, **34**, 241—251).—An address. Patterns in which silicate, phosphate, and borate groups combine to form polymers are illustrated and discussed. The formation of a complete series of solid solutions between $\text{Ba}_2\text{Si}_2\text{O}_7$ and $\text{Ba}_2\text{Si}_4\text{O}_{10}$ is explained as being due to addition of SiO_2 to the $(\text{Si}_2\text{O}_7)^{4-}$ chains of $\text{Ba}_2\text{Si}_2\text{O}_7$ to give the sheet polymer $(\text{Si}_4\text{O}_{10})^{4-}$ of $\text{Ba}_2\text{Si}_4\text{O}_{10}$. An illustration of the possible structural relation between cryst. B_2O_3 and cubic HBO_2 is given. Discussion of the types of silicate systems in which liquid immiscibility occurs shows that immiscibility results from mutual insolubility of space and sheet polymers arising from their greatly different configurations.

C. R. H.

System boron oxide-beryllium oxide-lithium oxide in glassy state. (Glasses transparent for X-rays.) L. J. Mazelev (*J. Appl. Chem. Russ.*, 1940, **13**, 1288—1303).—46 systems containing 2.5—15 wt.-% of BeO and 2.5—25% of Li_2O were examined. Transparent glasses are obtained at $\text{BeO} < 13\%$ when the wt. ratio $\text{Li}_2\text{O}:\text{BeO}$ is ~ 1 to 3. The softening interval of these glasses is very short; the softening temp. is $\sim 440^\circ$ for large [Li] and $\sim 500^\circ$ for small [Li]. d is the larger the smaller is [B], and is raised by Li more than by Be. Resistance to H_2O is small; it increases with [Be] and is lowered by B more than by Li. Thermal expansion increases with temp. and is the smaller the larger is [B]. n (1.52—1.57) is lowered by B and raised by Li. The crystals obtained on devitrification of the glasses had a composition near $2\text{BeO} \cdot \text{B}_2\text{O}_3$. The glasses BeO 14.08, Li_2O 17.66, B_2O_3 68.36 wt.-% and BeO 11.95, Li_2O 17.82, B_2O_3 70.23 wt.-% are recommended for windows in X-ray tubes.

J. J. B.

Thixotropy in silver amalgams. D. R. Hudson (*Physical Rev.*, 1944, [ii], **65**, 247—248).—There are small but definite peaks at 15% and 28% Ag in the density-composition curve. The sp. vol.-composition curve consists of straight lines intersecting at min. at 13% and 25%; thus the partial sp. vols. are const. for both components over corresponding ranges of composition. Amalgams containing $> 8\%$ of Ag are quite fluid although they are heterogeneous, the solubility of Ag in Hg being 0.03% at room temp. Over the range 8—20% Ag the amalgams are plastic, and set hard on keeping, but the hardened material recovers its plasticity on kneading. Possible explanations of this thixotropic effect are discussed.

N. M. B.

X-Ray study of the copper-manganese binary alloy system. L. D. Ellsworth and F. C. Blake (*J. Appl. Physics*, 1944, **15**, 507—512).—X-Ray analysis of slowly-cooled Cu-Mn alloys does not indicate superstructures but gives results inconsistent with Cu-Mn binary alloy equilibrium systems. Slowly cooled and annealed samples both show a series of continuous Cu-Mn solid solutions, showing a face-centred cubic lattice with a parameter increasing with [Mn] from 0 to 60%. With 60—90% Mn the lattice is face-centred tetragonal. With 90—100% Mn the system shows a solid solution with 90% Mn, and an α -Mn phase.

L. J. J.

Carbides in the iron-manganese-carbon system. E. Ohman (*Jernkont. Ann.*, 1944, **128**, 13—16; *Bull. Iron Steel Inst.*, 1944, No. 102, 60A).—An X-ray study made by the author in 1926 of the carbides present in the above system revealed a hitherto unknown double carbide of Mn and Fe which has a monoclinic crystal structure. By dissolution of C in molten Mn carbides are produced which, according to X-ray powder photographs, are isomorphous

with the Cr carbides Cr_{23}C_6 and Cr_7C_3 . As the powder photographs are in exact agreement with those obtained for the above Cr carbides the Mn carbides probably have the formula Mn_{23}C_6 and Mn_7C_3 . The latter has been observed only in alloys with $>80\%$ Mn, whilst Mn_{23}C_6 is found with up to 50% Fe and $<6\%$ C present. With $>80\%$ Fe cementite is the only carbide formed. Both cementite and Mn_{23}C_6 are present even when the Mn content is up to 70% . Mn can replace Fe in cementite to a considerable extent.

R. B. C.

Iron-nickel-aluminium-copper alloys with preferred magnetic orientation. W. Jellinghaus (*Arch. Eisenhüttenw.*, 1943, 16, 247—251; *Bull. Iron Steel Inst.*, 1944, No. 102, 54A).—A quinary Fe alloy containing Al 8—9, Co 23, Cu 3, and Ni 15% heat-treated in a magnetic field with subsequent tempering has preferred magnetic orientation and is the best known permanent-magnet material. A study was made of the structure and magnetic properties of a no. of alloys of the above composition except for Al, which varied between 5.7% and 16.7%. Specimens from all melts had as principal constituent one with a cubic body-centred structure. At the lower end of the Al range austenite was also present; only with the highest Al content was a cubic body-centred phase with superstructure observed. The temp.-coercivity relation showed that the intermediate, apparently homogeneous, structure consisted of >1 phase. The explanation of the permanent magnetism is the same as that in the case of ternary Fe-Ni-Al alloys. Heat-treatment in a magnetic field is effective only within a certain range of composition which is characterised by homogeneous solidification, a high Curie point, and the proximity of the solubility limit of austenite.

R. B. C.

Solubility of hydrogen in molten copper-tin alloys.—See B., 1944, I, 373.

Setschenov's rule and the solubility of hydrogen sulphide in hydrochloric acid solutions. A. F. Kapustinski and B. I. Anvaer (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 625—628).—The solubility of H_2S in HCl of concn. 16.5—34.9% has been determined. The results agree satisfactorily with the equation of Setschenov, $s = s_0 e^{kc}$, where s_0 = solubility of gas in H_2O , s = solubility in electrolyte, and c = concn. of electrolyte. The solubility does not pass through a min. The solubility of H_2S in HCl solutions of ZnCl_2 and FeCl_2 has also been determined. ZnCl_2 causes an increase and FeCl_2 a decrease in the solubility.

A. J. M.

Solubility of lithium carbonate. (Mlle.) L. Lagarde (*Compt. rend.*, 1943, 216, 156—158).—The solubility of Li_2CO_3 in the presence of Li^+ and of CO_3^{2-} has been determined by finding the solubility in presence of LiCl and of Na_2CO_3 . Addition of Li^+ gives an almost const. solubility product. The addition of CO_3^{2-} affects the solubility of Li_2CO_3 does that of LiCl .

A. J. M.

Properties of freshly formed surfaces. II. Rate of adsorption of isoamyl alcohol at air-water surface. C. C. Addison (*J.C.S.*, 1944, 252—256).—The vibrating jet technique (C., 1944, 43) has been used to study the rate of establishment of surface equilibrium of $\text{iso-C}_5\text{H}_{11}\text{OH}$ (I)— H_2O mixtures at air-liquid interfaces at 20° . From the variation in the lengths of successive waves in the jet the variation in γ with surface age has been deduced, and the velocity of migration of the (I) mols. to the surface calc. as $\sim 8.5 \times 10^{-4}$ cm. per sec. The slight decrease in this velocity with increasing concn. is attributed to mutual interference between migrating mols. Surface equilibrium is established in <0.025 sec. and ~ 0.01 sec. in 0.122 and 0.812% solution, respectively.

J. W. S.

Properties of freshly formed surfaces. III. Mechanism of adsorption, with particular reference to the sec.-octyl alcohol-water system. C. C. Addison (*J.C.S.*, 1944, 477—480).—The dynamic surface tension of aq. solutions of sec.- $\text{C}_8\text{H}_{17}\text{OH}$ and the mean velocity (V) at which the alcohol mols. migrate to the surface have been determined. Surface ages ranged from 0.01 to 0.12 sec. The mean val. of V is $>$ the val. for $\text{iso-C}_5\text{H}_{11}\text{OH}$ (cf. *supra*) and is independent of concn. The variations of V with the distance of the mol. from the surface and with the free energy of the surface are discussed. The free energy of the surface is shown to be the major factor determining V , the distance of the mol. from the surface being insignificant.

C. R. H.

Adsorption in relation to constitution. III. Adsorption of carbohydrates from aqueous solutions by charcoal. B. P. Gyani (*J. Indian Chem. Soc.*, 1944, 21, 79—82).—The adsorption by activated C of sugars from aq. solution is with SiO_2 gel. The adsorption coeff. increases in the order arabinose $<$ xylose $<$ fructose $<$ glucose $<$ galactose $<$ mannose $<$ rhamnose $<$ sucrose $<$ maltose, adsorption coeffs. of sugars of the same family being close together. Rhamnose shows anomalous behaviour since with a lower mol. wt. than the hexoses it should have a lower coeff. than the latter. The coeffs. for tri- and poly-saccharides are high (100% for maltin) and conform to the general rule that adsorption increases with mol. complexity.

C. R. H.

Kinetic studies of adsorption of phenol by activated carbon in packed towers. A. F. Tesi (*Univ. Pittsburgh Bull.*, 1944, 40, 303—310).—Adsorption of PhOH from its aq. solution by active C follows the Freundlich isotherm. In continuous flow through towers, the

Schumann-Furnas treatment of heat transfer can be applied to transfer of PhOH. A const. mass-transfer coeff. is obtained over a wide range of conditions.

L. J. J.

Efficiency of exchange, vapour pressure isotherms, and heats of wetting of technical hydrogen-ion exchangers. M. Trautz and H. Nienhaus (*J. pr. Chem.*, 1943, [ii], 162, 181—217).—The efficiency of exchange of H^+ with Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and Ba^{2+} solutions, and the dependence of the v.p. of H_2O over the solid and ΔH of wetting on the H_2O content of 3 commercial exchangers, have been determined.

W. R. A.

Thermodynamics and statistics of zeolitic solid solutions. R. M. Barrer (*Trans. Faraday Soc.*, 1944, 40, 374—384).—Occlusion isotherms are derived for solid solutions of the zeolitic type in which the occluded mols. possess various degrees of mobility within the lattice. Standard free energies and entropies of occlusion are calc., and compared with these quantities derived from experimental data. For various gas-zeolite systems, and for H_2 -M systems ($M = \text{Ti, Zr, Th, V, Pd}$), good agreement between experimental and calc. quantities is found if the occluded mols. or atoms are treated as three-dimensional oscillators; in these systems the possibility that any large fraction of the occluded mols. possesses even one degree of translational freedom is excluded. When long-chain mols. are occluded there is loss of three translational and three principal rotational degrees of freedom, and of numerous possible gas-phase configurations. A thermodynamic criterion for the formation of new phases is given.

F. L. U.

Surface tension of solutions. I. A. A. Shuchovitzki (*J. Phys. Chem. Russ.*, 1943, 17, 313—317).—If the mol. fraction of the solute is N , the surface tension of the solution is $\gamma_0 - RTn \log_e [1 + N(C - 1)]$, γ_0 being the surface tension of the solvent, n a function of the size of the mol., and C the work of displacing a mol. of solvent by a mol. of solute in the surface layer, which is supposed to be unimol.

J. J. B.

Calculation of the surface energy of non-polar substances from the heat of sublimation. R. Fricke (*Z. physikal. Chem.*, 1942, B, 52, 284—294; cf. A., 1943, I, 86).—A method is given for calculating the total and free surface energies of the various surfaces of a non-polar crystal from the surface energy obtained by Volmer *et al.*, from heat of sublimation at abs. zero. A special form of the third law of thermodynamics is developed for a series of cases, and the surface energies of a large no. of surfaces of metal crystals are evaluated. The total surface energy is const. over the whole range of accuracy of Dulong and Petit's law, and the free surface energy varies linearly with temp. over this range.

A. J. M.

Rate of rise of water in capillary tubes. W. A. Rense (*J. Appl. Physics*, 1944, 15, 436—437).—Assuming the flow to be turbulent, the rate equation for the rise of H_2O in a capillary tube is derived, viz., $z = k_1 + k_2 \log t$ (z = height, k = const., t = time). This agrees with measurements obtained by photographing the rise in stroboscopic light, except for points near the end of the rise when turbulence ceases. The possibility of determining the Reynolds no. dynamically from such observations is indicated.

J. H. Ba.

Formation of bubbles. R. B. Dean (*J. Appl. Physics*, 1944, 15, 446—451).—The efficiency of various substances as nuclei for the formation of gas bubbles is said to be due to the presence of absorbed or trapped gases. It is shown experimentally that many surfaces, when treated to remove such gases, lose their ability to form bubble nuclei. The very low pressures or high superheating necessary to produce gas bubbles in H_2O are compared with the ease of formation by mechanical shock or turbulent flow. Pressure-lowering in sound waves produced by shock is not sufficient to cause cavitation and hence bubbles, and it is suggested that disturbances give free vortices which produce sufficient tension to rupture the liquid.

J. H. Ba.

Wetting and swelling of graphite. P. Tschugunov and B. Bruns (*Acta Physicochim. U.R.S.S.*, 1943, 18, 351—357).—Measurements of the contact angle (α) of H_2 bubbles on the surface of polished graphite under $\text{n-H}_2\text{SO}_4$, -KCl , -KBr , -KI , -NaOH , and $\text{-Na}_2\text{SO}_4$ show that α_{max} occurs when the polarisation of the graphite is ~ -0.2 v. referred to the Hg_2Cl_2 electrode. The highest val. of α is 36° (in H_2SO_4) and the lowest 21° (in NaOH), the val. in the salt solutions being $\sim 28^\circ$. Graphite was treated with a mixture of H_2SO_4 and HNO_3 and excess of acid washed out of the swollen graphite. The amount of O_2 evolved on immersion in alkali is equiv. to the amount of fixed H_2SO_4 , assuming the formation of an acid salt. Similar results are obtained by anodic oxidation of graphite in $50\% \text{H}_2\text{SO}_4$.

C. R. H.

Surface viscosity and the structure of monolayers of higher alcohols. A. A. Trapeznikov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 321—326).— η of an octadecyl alcohol (I) monolayer was determined at various temp. The formula of Fourt and Harkins (A., 1938, I, 615) for η determined by a disc viscometer requires correction as the monolayer entrains measurable quantities of the substrate. The surface pressure (F) was also determined. The curves of η against F are given for monolayers of (I) on 0.01N-HCl, 0.01N-NaCl, and H_2O at different temp. The curves of F against area

per mol. (a) are also given. Since the F - a curves do not change their form to any great extent over a 10° range, it might be expected that the η - F curves would take identical courses at different temp. There is, however, a great difference in the form of the η curves at temp. between 15° and 22° . At low temp. the abs. η in the "solid" condensed state region ($F > 13.4$ dynes per cm.) is $<$ in the "liquid" state region ($F < 13.4$ dynes per cm.). η varies with F in a similar manner in both regions. After passing through a max. η rapidly decreases. The relation between F and η is very nearly linear for $F > 13.4$ dynes per cm. and at the lower temp. The position of the max. in the two pressure regions varies with temp. The divergence between contraction and expansion curves increases as temp. rises, but generally η is greater during expansion than contraction, especially at the transition boundary between the two regions.

A. J. M.

Pure and mixed monolayers of dilauryl maleate and fumarate. J. L. Shereshefsky and A. A. Wall (*J. Amer. Chem. Soc.*, 1944, **66**, 1072—1076).—The surface pressure-area relationships have been determined for dilauryl maleate and fumarate films at different temp. and for the mixed esters at 25° . The consts. in the Langmuir equation of state of duplex films for these substances have been evaluated. Area consts. agree with X-ray dimensions of maleic and fumaric acids. The relation between the val. of the dipole moment of the head group and the tendency to form expanded films and the relation between stability and surface potentials are discussed. Raoult's law can be applied to the pressure of head groups in mixed duplex films.

W. R. A.

Solutions of problems relating to media in contact by the method of wave-trains. G. Green (*Phil. Mag.*, 1944, [vii], **35**, 519—531).—Summations of wave-train effects for two media in contact are tabulated for the cases of a source in either medium or at the boundary. Applications are given to the solution of problems involving the transmission of elastic and thermal vibrations (cf. *ibid.*, 1940, [vii], **29**, 100).

H. J. W.

Theory of filtration of aerosols. I. Role of van der Waals forces. N. N. Tunitzkii and I. V. Petrianov (*J. Phys. Chem. Russ.*, 1943, **17**, 408—413).—It is assumed that between aerosol particles and solid surfaces an attraction exists which accelerates the filtration of aerosols through porous filters. The attraction is calc. for a force \propto (distance) $^{-6}$.

J. J. B.

Foaming properties of soap solutions.—See B., 1944, II, 320.

Use of low temperatures in the study of colloids. A. Boutaric (*Compt. rend.*, 1943, **216**, 379—380).—The stability of org. and inorg. colloidal solutions on storage is considerably greater at 0° than at higher temp.

L. J. J.

Examination of some carbons by X-ray diffusion at very small angles. H. Brusset, J. Devaux, and A. Guinier (*Compt. rend.*, 1943, **216**, 152—154).—Various specimens of C when examined by X-rays show a central diffusion spot as well as the rings due to graphite structure. This diffusion spot is characteristic of the disperse state, and if the intensity (I) diffused at angle ϵ is measured, the curve of $\log I$ against ϵ^2 tends towards a straight line for small ϵ . From the slope, a no. characteristic of the size of the particles can be obtained. Almost all the lignites examined gave a central diffusion spot. They contain micelles of various dimensions. Bitumen is intermicellar. A similar micellar dispersion was obtained for samples of anthracite. A sample of humic products, containing a large proportion sol. in bases, gave results very similar to those of lignite. Aq. solutions of NH_4 humate and of Na humate do not show the central diffusion spot. In the case of various active carbons the nature of the central spot varied considerably with the treatment. Activation causes breakdown into a very finely divided state.

A. J. M.

Viscosities of pectin solutions. H. S. Owens, H. Lotzkar, R. C. Merrill, and M. Peterson (*J. Amer. Chem. Soc.*, 1944, **66**, 1178—1182).—The relative η of pectin (I) solutions varies with concn. similarly to other ionisable hydrophilic colloids. In dil. solutions η attains a max. at pH ~ 6 but can be reduced to a min. by adding NaCl or an acid; $\text{CO}(\text{NH}_3)_2$ has little effect. As the concn. of (I) is increased to $>0.5\%$, the relative η is unaltered by varying pH between 1 and 7. The η -concn. curve follows the Arrhenius equation to $<0.1\%$ (I), when pH is 1 or 2 or when $<0.9\%$ of NaCl is present. This permits the calculation of vals. of intrinsic η which may have some relationship to mol. wt. The η -concn. curves for Na, NHMe , $\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{NH}_2$, $(\text{OH}\cdot\text{CH}_2)_2\text{CMe}\cdot\text{NH}_2$, and NEt_4 pectinates are practically identical. Temp. (0 – 50°) has little effect on η -concn. curves for solutions containing $<0.05\%$ of (I), but above 0.05% η decreases with rising temp. A tentative explanation is advanced.

W. R. A.

Viscosimetric determination of the degree of polymerisation and the shape of polyamides in solution. A. Matthes (*J. pr. Chem.*, 1943, [ii], **162**, 245—278).—The relation between intrinsic viscosity, $[\eta]$, and degree of polymerisation, P , of an ϵ -aminohexolactam polyamide (I) has been determined in conc. and 40% aq. H_2SO_4 ; $[\eta] = KP^a$ (K and a are consts.), $K = 0.0281$, $a = 0.668$ in conc. H_2SO_4 , $K = 0.0268$, $a = 0.510$ in 40% aq. H_2SO_4 . The relation

has been used in a viscosimetric study of the depolymerisation of (I) in 40% aq. H_2SO_4 . All available evidence points to a long unbranched and coiled chain as the shape of polyamide mols. The amount of coiling varies with the solvent.

W. R. A.

Electrical and elastic properties of amorphous polar polymers. R. F. Tuckett (*Trans. Faraday Soc.*, 1944, **40**, 448—462).—The deformation of an amorphous polymer under const. stress is examined theoretically with reference to a spring-dashpot model, and it is shown that, whilst the rate of ordinary elastic deformation is characterised by a true relaxation time related to the ordinary macroscopic viscosity, the rate of highly elastic deformation is characterised by an "orientation time," τ , as expressed by $D_t = D_\infty(1 - e^{-t/\tau})$, which is related to the modulus of high elasticity by a friction const. that is \ll the ordinary viscosity and to which no definite physical meaning can be assigned. In this latter respect the theory diverges from Debye's treatment of dipole rotation. If a dipole is attached to the main chain in an amorphous polymer, both dipole rotation and highly elastic orientation are affected to the same extent by intermol. forces, and both processes should have the same time consts. This hypothesis is supported by some experimental evidence and by a consideration of energies of activation of various mol. rate-processes. Orientation-time distributions are also discussed.

F. L. U.

Interaction between rubber and liquids. V. Osmotic pressures of polymer solutions in mixed solvents. VI. Swelling and solubility in mixed liquids. G. Gee (*Trans. Faraday Soc.*, 1944, **40**, 463—468, 468—480).—V. An expression is obtained for the free energy of dilution of a ternary mixture of polymers + two liquids by one of the liquids, and is applied to the osmotic equilibrium between a solution of a polymer in the two liquids and a second phase containing only the two liquids. The osmotic behaviour of the ternary solution is very similar to that of a solution of the polymer in a single liquid, and van 't Hoff's law holds at infinite dilution. The distribution of the two liquids in the solvent and solution phases is calc. This is identical only if the heat of mixing of the three components is zero and if the two liquids have equal mol. vols., whilst for fairly large heats of mixing the % difference between the mol. ratio of the liquids in the two phases may be of the same order as the vol.-% of polymer in the solution.

VI. The solvent properties of a mixture of two liquids are intermediate between those of the constituents only when these mix ideally; the larger is the heat of mixing, the greater is the solvent power of the mixture relative to those of the components. Hence over a certain concn. range a mixture of two non-solvents may be a solvent. The same principle applies to the swelling of a cross-linked polymer. Methods of estimating the val. of the consts. in the equations derived in the preceding paper are discussed. Experimental data for the crit. solubility limits of unvulcanised rubbers and the swelling of vulcanised rubbers are semi-quantitatively explained from the measured heats of mixing of the three binary mixtures, and qualitatively from the cohesive energy densities of the three separate components.

F. L. U.

Ordered swelling state of nitrocellulose. G. V. Schulz (*Z. physikal. Chem.*, 1942, **B**, **52**, 253—256).—If the effect of concn. of cellulose nitrate (I)— COMe_2 mixtures on the entropy of swelling is determined, it is found that the entropy is negative for a degree of swelling (q) (vol. to which 1 c.c. swells) <3 , and positive above that. This is in agreement with the work of Kratky, Sekora, and Treer, who have shown that at comparatively high q of (I) in COMe_2 , definite lattice structures exist, as shown by X-ray analysis. The upper limit for the occurrence of these structures is $q \sim 3$. The limit between the two regions appears also in mechanical properties of the mixture. The process of swelling can be explained on the basis of these observations. For comparatively small amounts of the swelling agent, the forces between the components are strong enough to maintain the solid, lattice arrangement. With the addition of more of the swelling agent, the distances between the components increase, the binding energy of the (I) mols. decreases, and the lattice breaks down.

A. J. M.

Structure and properties of cellulose ester films. II. Structure change of cellulose nitrate films during their relaxation. V. A. Kargin, P. V. Kozlov, and R. V. Zueva (*J. Phys. Chem. Russ.*, 1943, **17**, 318—325).—When cellulose nitrate films (from COMe_2) were stretched and then released, a part (about $\frac{1}{2}$) of their birefringence disappeared rapidly (some hr. at room temp., and some sec. at 100 – 150°) but the rest of it remained for days. The orientation shown by X-rays was permanent at room temp. but disappeared at 100 – 150° . Stretched and then released benzylcellulose films lost their birefringence completely after heating at 100° ; no orientation as shown by X-rays occurs in these films. It is concluded that relaxation of stretched films takes place in two distinct stages.

J. J. B.

Kinetics of isothermal coagulation of non-colliding particles. N. N. Sirota (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **40**, 234—238).—Mathematical. The isothermal coagulation of a solid dispersion phase (spheroidal cryst. particles) dispersed in a solid

matrix is regarded as consisting of dissolution of the particles of the disperse phase and their growth. W. R. A.

Electrokinetic phenomena in relation to electrodialysis. I. I. Shukov (*Uspechi Chim.*, 1943, 12, 265—286).—The transference no. of Cl^- in KCl is not affected by collodion membranes with large pores (radius $r > 10^{-5}$ cm.), but is reduced to < 0.3 when r is $< 10^{-7}$ cm. For a given r the reduction is the larger the more dil. is the KCl solution; this is explained by a contraction of the double layer in higher concn. The ζ -potential has a max. when $r = 10^{-5}$ cm. and is very small at $r < 10^{-7}$ cm.; it is a definite function of the permeability of the membrane for H_2O . For electrodialysis the transference nos. n in the membranes are more important than the ζ -potentials. According to the vals. of n in the membranes of a two-membrane electrodialyser the middle portion can be diluted or conc. Positive collodion membranes are obtained by incorporating in the collodion quinine or nigrosine, and negative ones, by incorporating Baden-blue. The smaller is r , the larger is the difference between the n of different ions. J. J. B.

VI.—KINETIC THEORY. THERMODYNAMICS.

Fugacities in gas mixtures. M. Temkin (*J. Phys. Chem. Russ.*, 1943, 17, 414—423).—A thermodynamic equation for the fugacity of a component of a gas mixture is derived; it can be applied if the pressure of the mixture is known as a function of temp., vol., and composition. Solutions are given for equations of state of the van der Waals and Kammerlingh-Onnes types. J. J. B.

Dimerisation in perfect solutions. Analysis of data of Brown and Bury. W. F. K. Wynne-Jones and G. S. Rushbrooke (*Trans. Faraday Soc.*, 1944, 40, 345—352).—The cryoscopic measurements by Brown and Bury (cf. A., 1926, 676) for several solutes in dry PhNO_2 are reconsidered. By avoiding one approximation used by these authors in their calculations, and by using a new formula involving activity coeffs., evidence is obtained for dimerization of acids (EtCO_2H , $\text{CH}_3\text{Ph}\cdot\text{CO}_2\text{H}$) and probably of $\beta\text{-C}_{10}\text{H}_{17}\text{OH}$, but not of alcohols ($\text{CH}_3\text{Bu}^n\text{OH}$, $\text{CH}_3\text{Ph}\cdot\text{OH}$). F. L. U.

Properties of reversible micelle formation from the viewpoint of the law of mass action. O. Lamm (*Arkiv Kemi, Min., Geol.*, 1944, 18, A, No. 9, 22 pp.).—The theory of simple micelle formation (the aggregation of low-mol. particles with increasing concn.) is developed on the basis of the law of mass action. The more complex case where the equilibrium const. varies with particle size is also considered, assuming a statistical distribution of particle size. If for a given concn. there is a statistical distribution of particles, this is true for all concns. Sedimentation and diffusion and their connexion with micelle formation are discussed. The treatment is applied only to non-electrolytes. A. J. M.

Strengths of six monocarboxylic acids in 25% aqueous acetone and 20% aqueous sucrose. I. Davey and J. F. J. Dippy (*J.C.S.*, 1944, 411—415).—Dissociation consts. at 25° have been determined by a conductivity method for EtCO_2H , BzOH , $\text{CH}_3\text{Ph}\cdot\text{CO}_2\text{H}$, $\text{CHPh}_2\cdot\text{CO}_2\text{H}$, $\text{Ph}(\text{CH}_2)_2\cdot\text{CO}_2\text{H}$, and $\text{CHPh}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$. With the exception of $\text{CHPh}_2\cdot\text{CO}_2\text{H}$, the order of strengths is the same as for aq. solutions. The strengths in aq. sucrose are $>$ those in H_2O despite the lower dielectric const. of the sucrose solution. $\text{CHPh}_2\cdot\text{CO}_2\text{H}$ is anomalous since the strength in aq. CMe_2 is $<$ instead of $>$ that of BzOH , and the strength in aq. sucrose is $<$ in H_2O . C. R. H.

Binary system $\text{P}_2\text{O}_5\text{--}2\text{CaO}\cdot\text{P}_2\text{O}_5$. W. L. Hill, G. T. Faust, and D. S. Reynolds (*Amer. J. Sci.*, 1944, 242, 457—477).—Data from quenching experiments are recorded and phase diagrams presented for the equilibrium relationships between P_2O_5 and $\text{Ca}_2\text{P}_2\text{O}_7$. Eight cryst. phases are stable at liquidus temp., viz., tetragonal (?) (P_2O_5)₈ with a triple point at 580° and 555 mm.; $\text{CaO}\cdot 2\text{P}_2\text{O}_5$, m.p. 810° ; $2\text{CaO}\cdot 3\text{P}_2\text{O}_5$, incongruent m.p. 774° ; $\beta\text{-CaO}\cdot\text{P}_2\text{O}_5$, m.p. 977° (metastable); $\alpha\text{-Ca}$ metaphosphate, m.p. 984° ; tremelite, observed as a series of solid solutions ranging from ~ 32 to 37% CaO , which is metastable below 915° and melts incongruently at 985° ; $\beta\text{-}2\text{CaO}\cdot\text{P}_2\text{O}_5$; and $\alpha\text{-}2\text{CaO}\cdot\text{P}_2\text{O}_5$, m.p. 1353° . The $\alpha \rightleftharpoons \beta$ inversion points of $\text{CaO}\cdot\text{P}_2\text{O}_5$ and $2\text{CaO}\cdot\text{P}_2\text{O}_5$ lie at 963° and 1140° , respectively. L. S. T.

Three-phase pressures for solid salt-solution-vapour. I—III. (Miss) A. E. Korvezee and P. Dingemans (*Rec. trav. chim.*, 1943, 62, 625—638, 639—652, 653—657).—I. The "characteristic coeff." (k) of Kume (A., 1936, 1197) depends on temp. and is therefore not a characteristic const. for each substance. This variation may be small (resorcinol) or large (NaBr), and is related to the variation of the activity of H_2O with the molar concn. Moreover, discontinuities in the k -temp. curves occur at transition temp. The v.p. of the saturated solutions relative to that of pure H_2O at the same temp. varies approx. linearly with temp. along the three-phase pressure curves. An expression is given for the activity of the H_2O in the saturated solution in terms of the relative v.p.

II. For salts having two cryst. forms with a transition temp. there are three types of pressure-temp. curves possessing either two stable max. or one stable and one metastable max. Equations are given for the relative v.p.-temp. curves for three saturated

solutions, from which the max. in the pressure-temp. curves can be calc. with an accuracy $\sim 1\%$. The heat of transition between two cryst. forms can be obtained from the differences in slopes of the relative v.p. curves at the transition temp., and also from the difference in the heat of crystallisation of the two forms at the temp. of the max. Data and calculations are given for the systems $\text{H}_2\text{O--NH}_4\text{NO}_3$, $\text{H}_2\text{O--AgNO}_3$, and $\text{H}_2\text{O--KCNS}$ which exemplify the three types mentioned.

III. Expressions are derived for ideal systems connecting the m.p. of substance and the temp. at which a max. occurs on the three-phase pressure curve solid-saturated solution-vapour, and for the distances between the temp. of the two max. on the three-phase pressure curves when the solid occurs in two modifications. Compared with all the known systems salt- H_2O , they show an error $\sim 1\%$. J. O'M-B.

Mineralogical aspects of the system $\text{FeO--Fe}_2\text{O}_3\text{--MnO--Mn}_2\text{O}_3$. B. Mason (*Stockholms Hogsk. Min. Inst., Rept.* 150; *Geol. Foren. i Stockholm Forh.*, 1943, 65, 97—180; *Bull. Iron Steel Inst.*, 1944, No. 102, 32A).—Chemical, physical, and mineralogical studies of the system were made to determine the phase relations with the view of defining the limits of the different mineral species and elucidating their mutual relations. The mineral species in the system are: magnetite, Fe_3O_4 ; hematite, $\alpha\text{-Fe}_2\text{O}_3$; maghemite, $\gamma\text{-Fe}_2\text{O}_3$; manganosite, MnO ; hausmannite, Mn_3O_4 ; bixbyite, $\alpha\text{-Mn}_2\text{O}_3$, with up to $\sim 60\%$ of Fe_2O_3 in solid solution; jacobite, $(\text{Fe,Mn})_3\text{O}_4$ (Mn_2O_3 16.7—54%); and vredenburgite $(\text{Mn,Fe})_3\text{O}_4$ (Mn_2O_3 54—91%). The literature is critically reviewed. R. B. C.

Application of free energy equations to the study of the synthesis of hydrocarbons from carbon monoxide and hydrogen. W. W. Myddleton (*J. Inst. Petroleum*, 1944, 30, 211—224).—The vals. of the consts. A , B , etc. and of the integration const. (I) in the general free energy equation $\Delta G_T = \Delta H_0 + AT \log_e T + BT^2 + CT^3 + \dots + IT$, where ΔH_0 is regarded as the change in heat content in hypothetical reaction at abs. zero, have been calc. from known thermal data and derived equations for the reactions $n\text{CO} + (2n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + (2 + n)\text{H}_2\text{O}$ and $2n\text{CO} + (n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{CO}_2$ over the range $25\text{--}250^\circ$. Terms in D contribute $< 0.1\%$, those in $C + D < 2\%$, and those in $B + C + D < 10\%$ to the total free energy. Vals. for the latter are given for the lower paraffins and olefines. The reaction in which CO_2 is formed has a higher negative free energy than that producing H_2O , and the formation of CO_2 would be expected to accompany the latter reaction. Special conditions at the catalyst surface are suggested as a reason for the inhibition of CO_2 formation. CO may be adsorbed by the catalyst by either dual attachment, when H_2O is formed by reaction with H_2 , or single attachment, when H_2 forms CO_2 and CH_2 groups which are converted into CH_4 by the action of chemisorbed H . Dual attachment does not occur with Fe catalyst. The appearance of traces instead of large amounts of C_2H_4 is accounted for by the incorporation of C_2H_4 actually formed into the building up of hydrocarbon chains. The free energy relations predict appreciable quantities of *iso*-paraffins, and modifications in catalyst and in reaction conditions may be able to increase the yield. Conditions which favour aromatic hydrocarbon formation are less likely to be attained. C. R. H.

Bond energy of organic compounds. J. K. Sirkin (*J. Phys. Chem. Russ.*, 1943, 17, 347—380).—The heats of formation of org. compounds are discussed. They can be considered as sums of bond energies; new vals. for these energies are calc. They often appear to be identical in compounds in which the lengths of the bond are different, and sometimes they are different in compounds having equal bond lengths (e.g., in lower and higher paraffin hydrocarbons). The groups CHMe or CMe_2 have a greater energy content than $\cdot\text{CH}_2\cdot\text{CH}_2\cdot$ or $\cdot\text{CH}\cdot\text{CH}_2\cdot$. The largest deviations from additivity are due to resonance. J. J. B.

Thermochemistry of formaldehyde, hexamethylenetetramine, and their derivatives. M. Delpeine and M. Badoche (*Compt. rend.*, 1942, 214, 777—780).—Heats of combustion have been redetermined by an accurate bomb method, giving the following mol. vals. at const. vol. and const. pressure: $\frac{1}{3}(\text{CH}_2\text{O})_3$ 120.9, 120.9; $1/n(\text{CH}_2\text{O})_n$ (polyoxymethylene) 120.3, 120.3; $\frac{1}{6}[(\text{CH}_2\text{O})_6\cdot\text{H}_2\text{O}]$ 120.05, 120.05; $(\text{CH}_2)_6\text{N}_4$ 1003.0, 1003.6; $(\text{CH}_2)_6\text{N}_4\cdot 2\text{HNO}_3$ 953.6, 952.2; $\text{C}_6\text{H}_{10}\text{O}_4\text{N}_6$ (dinitrosopentamethylenetetramine) 866.1, 865.2; $\text{C}_6\text{H}_8\text{O}_4\text{N}_6$ (trinitrosotrimethylenetetramine) 557.9, 556.2; $\text{C}_6\text{H}_8\text{O}_4\text{N}_6$ (trinitrotrimethylenetetramine) 506.6, 503.9 g.-cal. L. J. J.

Heats of transformation in the systems wurtzite-sphalerite, and cinnabar-metacinnabarite. A. F. Kapustinski and L. G. Tschentzova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 489—490).—The heats of dissolution of synthetic wurtzite and sphalerite in HCl have been determined by means of an adiabatic calorimeter to be 17.4 and 50.2 g.-cal. per g., respectively. These vals. give 3190 g.-cal. per g.-mol. for the heat of transformation ZnS (sphalerite) \rightarrow ZnS (wurtzite). The heats of dissolution of synthetic cinnabar and metacinnabarite in aq. K_2S (38%) and KOH (2%) were 12.4 and 16.5 g.-cal. per g., respectively, giving 950 g.-cal. per g.-mol. for the heat of transformation HgS (cinnabar) \rightarrow HgS (metacinnabarite). A. J. M.

Exact calculation of heats of dissolution from solubility data. A. T. Williamson (*Trans. Faraday Soc.*, 1944, 40, 421–436).—Exact thermodynamical treatment leads to the general equation $\Delta H - \nu RT^2(dm/dT)_{\text{sat.}}[(\partial \log \gamma / \partial m)_T + (1/m)_{\text{sat.}}]$ for the heat of dissolution, where ν is the no. of ions per mol. of an electrolyte, m is the molality of the saturated solution, and γ the mean activity coeff. of an electrolyte (for non-electrolytes $\nu = 1$ and $\gamma = f_2$, the fugacity of the solute). Vals. of ΔH calc. from data for KCl, Ba(NO₃)₂, Na₂CO₃, NaOH, and CO(NH₂)₂ agree well with calorimetric determinations. An appendix contains alternative forms of the equation for use with different kinds of experimental data (solvent activities, osmotic coeffs.) and for solvated solutes.

F. L. U.

Energies of solution of silica in water and hydrochloric acid. P. G. Nutting (*J. Chem. Physics*, 1944, 12, 347–348).—Energy relations relating to Si(OH)₄ solutions are calc. from the solubility of pure SiO₂ in H₂O and HCl solutions. Most of the energy change is due to the first H₂O taken on during hydration of the SiO₂, the second H₂O differing little in energy from the solvent.

L. J. J.

Calorimetric study of the absorption of acetone by β -methylglucose tetranitrate and β -methylcellobiose heptanitrate. E. Calvet and A. Maurizot (*Compt. rend.*, 1943, 216, 51–52).—The heat of absorption of COMe₂ by β -methylglucose tetranitrate (I) and β -methylcellobiose heptanitrate (II) has been determined. The results are expressed as the amount of heat given out when n mols. of COMe₂ attach themselves to a C₆ group. For $n < 1$, (I) and (II) adsorb COMe₂. For $n = 1$, a liquid phase appears. The solid phase disappears when $n = 5$ for (I), and when $n = 3$ for (II). The curve of heat of adsorption against n is linear up to $n = 3$, and there is a max. at $n = 6$ for both (I) and (II). This max. is 5750 g.-cal. for (I) and 5400 g.-cal. for (II). The heat of dissolution per C₆ group is –4000 g.-cal. for both. Comparison is made with the results for the cellulose nitrates (III), where a max. is also obtained for $n = 6$. The form of the curve of heat of absorption against n is also the same, but in the case of (III) the max. heat evolved is ~4 times > that for (I) and (II), and the total heat of dissolution is positive. The difference is due to the fact that (I) and (II) are cryst., and dissolve readily in COMe₂, the dispersion in the solvent (negative thermal effect) taking place at the same time as gelatinisation (positive effect), whereas in (III) the dispersion does not occur at the outset of gelatinisation.

A. J. M.

VII.—ELECTROCHEMISTRY.

Electrical conductance of aqueous solutions. I. Sodium and potassium bromates at 25°, and the conductance of the bromate ion. J. H. Jones (*J. Amer. Chem. Soc.*, 1944, 66, 1115–1116).—Vals. of Λ have been measured at 25° for aq. KBrO₃ (0.0005–0.15M.) and aq. NaBrO₃ (0.0005–0.5M.) and ρ of aq. NaBrO₃ (0.0005–0.3M.) have been determined at 25°. Λ_0 for BrO₃' at 25° is 55.78 ± 0.05.

W. R. A.

Electrical conductivity of the thoria-ceria system. M. Foex (*Compt. rend.*, 1943, 216, 443–445).—The conductivity of ThO₂-CeO₂ mixtures has been measured at 800° and 1200° in atm. of O₂, N₂, and H₂, and in a vac. Max. resistivity is found with 1 mol.-% CeO₂ in N₂ and in a vac.; in O₂ a flat max. exists with 1–2 mol.-% CeO₂, whilst in H₂ no max. is found, the resistivity decreasing continuously with increasing [CeO₂]. Outside this range resistivity decreases with increasing [CeO₂] in all cases, but in O₂ that of CeO₂ is slightly decreased by addition of 1–5 mol.-% ThO₂.

L. J. J.

Physical properties of isomeric oximes. I. Molecular conductivities in liquid sulphur dioxide of isomeric aldoximes. N. K. Patwardhan and S. S. Deshpande (*J. Indian Chem. Soc.*, 1944, 21, 135–138).—Mol. conductivities for liquid SO₂ solutions of benzaldoxime and its *o*-, *m*-, *p*-NO₂- and *p*-OMe-derivatives and of furfuraldoxime and cinnamaldoxime have been measured. The β -aldoximes have higher conductivities than the α -aldoximes, suggesting that the β -forms are "anti" and the α -forms "syn."

C. R. H.

Effect of adsorbed layers of molecules of dielectrics on the contact potential difference between two metals. J. H. von Duhn (*Ann. Physik*, 1943, [v], 43, 37–52).—Contact p.d. of Ni, Cu, Ag, Ta, and Pt surfaces, saturated with vapours of paraffins, aliphatic alcohols, and C₆H₆, PhMe, and PhCl at a pressure of 2–10^{–4} mm. Hg, and measured against a normal electrode, are ~ ± 0.8 v. The p.d. varies with the adsorption pressure, the electron structure of the metal, and the mol. refraction of the adsorbate, but not with the dipole moment of the latter.

L. J. J.

Applicability of Nernst formulæ to amphoteric adsorbents. A. N. Frumkin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 417–419).—The p.d. between the surface of an amphoteric non-conducting adsorbent and the solution can be expressed by the same relation as for a H electrode provided that the no. of adsorbing groups on the surface is great enough.

W. R. A.

Theory of hydrogen ion discharge. III. Palladium. A. Frumkin and N. Aladjalova (*Acta Physicochim.*, 1944, 19, 1–35).—The properties of Pd electrodes depend largely on the nature of the

surface. Experimental results indicate that the overvoltage of Pd during evolution of H consists of two parts. One of them is almost independent of the nature of the solution, and is slowly attained after switching on the current. It also disappears slowly when the current is switched off, and can be transmitted to the diffusion side of the electrode. This indicates that it is an equilibrium potential between H₂ dissolved in the metal and that in the electrolyte. The other part of the overvoltage, which may reach high vals. in alkaline solutions, is not connected with evolution of H, but depends on the electrochemical reaction itself quite apart from the electrodes. This overvoltage is not affected by transition of Pd from the α to the β phase. It is independent of the area of Pd covered by the H₂. The mechanism of the process accounting for these facts is based on the theory of slow discharge. Equations are deduced showing the overvoltage to be composed of two parts, one depending on the intensity of current, the other on the equilibrium potential of adsorbed H₂, in accordance with the experimental facts. The theories of Farkas (A., 1937, I, 75, 253) and of Hickling *et al.* (A., 1943, I, 18) are discussed in the light of the experimental results. The poisoning of Pd electrodes is briefly considered.

A. J. M.

Effect of temperature on the discharge of N₃' ions and OH' ions in solutions of azides. E. T. Verrier (*Compt. rend.*, 1943, 216, 183–185; cf. A., 1942, I, 268).—In order to confirm the equation $\Delta N = kK_A e^{-W/RT} e^{VI}$ (K_A is a factor depending on the principal optical absorption of HN₃, W is energy of activation of the photogenic reaction, V — potential, I — intensity of current) for the intensity (ΔN) of the ultra-violet ray emitted at the anode in the electrolysis of HN₃ and NaN₃, the effect of temp. on the radiation has been investigated. The curve of log (K/K_A) against ($1/T$) ($K = kK_A e^{-W/RT}$) shows two straight lines separated by discontinuities at 12° and 18°. The slopes of these lines give energies of activation of 9500 g.-cal. (0–12°) and 5500 g.-cal. (18–40°). It appears that OH' alone are discharged at temp. < 12° and N₃ only above 18°.

A. J. M.

Influence of the anion on the capacity of a mercury electrode in dilute solutions. M. Vorsina and A. Frumkin (*Acta Physicochim. U.R.S.S.*, 1943, 18, 341–350).—As an extension of an earlier investigation (cf. A., 1944, I, 245) the capacity (C) of a Hg electrode in solutions of H₂SO₄, NaOH, Na₂SO₄, HCl, KCl, HBr, and KBr has been measured. The val. of $C_{\text{min.}}$ is > the val. calc. according to the Stern double layer theory when sp. adsorption is neglected. The magnitude of $C_{\text{min.}}$ and the corresponding val. of the potential depend on the adsorbability of the anion, increase in the latter being accompanied by an increase in $C_{\text{min.}}$. Where anion adsorption is strong, as, e.g., with appreciable concns. of I', $C_{\text{min.}}$ disappears altogether.

C. R. H.

Polarographic reduction of rhodium compounds. J. B. Willis (*J. Amer. Chem. Soc.*, 1944, 66, 1067–1069).—Rh complexes formed between RhCl₃ and KCN, KCNS, KCl + C₆H₅N, and NH₄Cl are stable towards Hg and give well-defined polarographic steps. Each reduction takes place from Rh^{III} to Rh^{II} and in no case, except possibly with KCNS, was the Rh^{III} → Rh step observed. There is evidence that the reducible ions formed are [Rh(CN)₅]^{3–}, [Rh(CNS)₃]^{3–}, [Rh(C₆H₅N)₃]^{3–}, and [Rh(NH₃)₃Cl]^{3–}. Some Rh complexes show no polarographic steps.

W. R. A.

Reduction of quinaldine acid at the dropping mercury cathode. J. T. Stock (*J.C.S.*, 1944, 427–430).—Current-voltage curves of 0.001M-quinaldine acid (I) in well-buffered aq. solutions at 25° over the pH range 1.5–12 have been obtained. (I) is reducible over the entire range, the principal product being dihydroquinaldine acid. At low pH the curves consist of two waves separated by a max. As pH is increased the lower wave is shifted towards more negative potentials, the upper wave decreases in height, finally vanishing at pH 4, and the max. broadens. This max. can be completely suppressed by addition of 0.02% of gelatin, but at the same time the lower wave moves to more negative potentials and the upper wave disappears. Up to pH 6 the relation $E_{\frac{1}{2}} = -(0.52 + 0.06\text{pH})$ v. holds for the lower wave. The height of the wave is \propto concn. of (I), and measurement of wave heights provides a means of determining (I) polarographically.

C. R. H.

Polarographic investigation of cysteine, glutathione, and ascorbic acid. R. G. Rieser (*Univ. Pittsburgh Bull.*, 1944, 40, 220–226).—Half-wave potentials and diffusion coeffs. for reduction of cysteine and oxidised glutathione are calc. from polarographic data. The latter gives normal diffusion current-voltage curves from pH 9.3 to 2N-H₂SO₄. At pH 1.0 and 2.2 the diffusion current is \propto the concn. Dehydroascorbic acid does not give a reduction polarogram at pH 3.1–10.6. Reduction of cysteine and dithiodiglycolic acid shows similar mixed potential polarograms. CH₂I-CO₂H with the appropriate thiol compound at pH 1.0 gives a quant. yield of oxidised glutathione and a 90% yield of cysteine.

L. J. J.

Ohmic resistance of local cells in the process of dissolution of metals in acids. B. Levitsch and A. Frumkin (*Acta Physicochim. U.R.S.S.*, 1943, 18, 325–340).—The conditions determining the behaviour of the cathode of a local cell are considered on the assumptions that the cathode is an inclusion having the shape of a disc, anode potential is zero, anode polarisation is neglected, and the

cathode is strongly polarised. The max. sp. resistance per unit area opposed to the current flowing to the centre of the cathode disc is $2r_0/\pi\chi$, where r_0 is the radius of the disc and χ is the conductivity of the electrolyte. As examples, the effect of inclusions of Sb in Pb and Ni in Zn when H_2SO_4 is the solvent has been calc. In the first case the ohmic potential drop may be neglected even for large inclusions and in the second it is ≥ 13 mv. if r_0 is $\sim 10^{-4}$ cm. Where the ohmic potential drop cannot be neglected, changes in electrolyte concn. at the cathode surface should be taken into account.

C. R. H.

Graphical method of calculating polyelectrode electrochemical systems as applied to corrosion processes. N. D. Tomaschov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 621–623).—Comparison of cathode and anode polarisation curves makes it possible to calculate the work of each separate electrode in a polyelectrode system with any no. of electrodes. The relative surface area of each electrode in the system must be known, and the cathode and anode polarisation curves (c.d. against potential) under conditions close to the working conditions of the system must be plotted for each component of the system separately. The assumption is then made that the effective potentials of all the electrodes of the system become equal as the result of polarisation. This is usually the case if the total ohmic resistance is small. The c.d.-potential curves are replotted on a general current-potential diagram. The general potential of the system is the potential at which the sum of all the cathode currents equals the sum of all the anode currents. The curve indicates which electrodes will act as cathodes and which as anodes. In some cases the polarisation curves for the individual electrodes can be calc. but they usually have to be obtained experimentally.

A. J. M.

VIII.—REACTIONS.

Explosives reactions. I. Chain reactions and gaseous explosions. M. F. R. Mulcahy and A. Yoffe (*J. Proc. Austral. Chem. Inst.*, 1944, 2, 106–120).—An introduction to the theory of chain reactions and gaseous explosions.

C. R. H.

Temperature gradients in gaseous explosions. A. S. Leah (*Nature*, 1943, 152, 303–340).—Mean gas temp. in the burnt portion of explosive mixtures may be obtained by photographically recording flame travel and simultaneously measuring pressure rise by a diaphragm type of indicator; a large spherical explosion vessel, with central ignition, is used. Experiments with 10% O_2 + 90% CO indicate a rise in temp. as the flame travels outward from the spark, thus confirming David's theory that the latent energy decreases in the same direction.

E. R. R.

Temperature of flame gases. W. T. David (*Nature*, 1943, 152, 278).—Considerable differences in temp. indicated by thermometric substances immersed in CO-air and CH_4 -air mixtures are observed when bare and quartz-covered Pt-Rh wires were used. The differences are largely due to the recombination of abnormally dissociated products on the surface of the wire. In CO-rich mixtures this effect is apparently suppressed.

E. R. R.

Theory of slow combustion. L. Landau (*Acta Physicochim.*, 1944, 19, 77–85).—The transference of heat from burning products of combustion to unburnt gas is usually assumed to be by simple thermal conduction. The stability of such a system is considered, and it is shown that the above assumption is not justified, as convection also plays a dominating part. The combustion of liquids is also considered.

A. J. M.

Ignition of carbon and kinetics of its reaction with oxygen. Z. Klibanova and D. Frank-Kamenetzki (*Acta Physicochim. U.R.S.S.*, 1943, 18, 387–405).—The kinetics of the reaction between C and O_2 at ordinary pressure and at high temp. have been measured by a method based on the determination of the temp. which a C filament must attain before it ignites in a stream of air or other O_2 -containing gas. The abs. reaction velocity at $\sim 1200^\circ\text{K}$. is $\sim 10^{-4}$ mol. per c.c. per sec., a val. of the same order as is obtained by other methods. The present data show a temp.-dependence which suggests an activation energy energies previously reported. The present val. is 75–135 kg.-cal. per mol., corresponding with a reaction order 0.4–0.8, and definitely < 1 .

C. R. H.

Oxidation of carbon. Z. F. Tschuchanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 32–36).—Velocities of oxidation of electrode C at 720 – 770°K . (Chaikina, A., 1938, I, 628) correspond with energies of activation 43,000 and 37,000 g.-cal. per g.-mol. for the reactions $3\text{C} + 2\text{O}_2$ (ads.) = C_3O_4 and $\text{C}_3\text{O}_4 + \text{C} + \text{O}_2$ (gas) = $2\text{CO} + 2\text{CO}_2$, respectively. Corresponding vals. from the velocity of oxidation of active wood charcoal (Tschuchanov, A., 1941, I, 272) at 873 – 973°K . are $\sim 19,000$ and $\sim 27,000$ g.-cal. per g.-mol. Divergent results obtained by other authors in different temp. ranges are explained by the simultaneous variation of the velocity coeffs. of the above two reactions with temp.

L. J. J.

Reaction of unsaturated halides with sodium vapour. A. G. Evans and H. Walker (*Trans. Faraday Soc.*, 1944, 40, 384–397).—Speeds of reaction of a no. of org. halides with Na have been measured, and the velocity coeffs., together with calc. collision nos.

and activation energies, are recorded. In many cases the velocity is $>$ would be expected from the corresponding C-halogen bond strength, and the possibility of accounting for these anomalies by extra resonance forms in the transition state is discussed. F. L. U.

Kinetics of anionotropic rearrangement. I. Rearrangement of propenylethynylcarbinol. E. A. Braude and E. R. H. Jones. **II. Medium effects in the oxotropy of propenylethynylcarbinol. Determination of isodielectric energies of activation.** E. A. Braude (*J.C.S.*, 1944, 436–443, 443–449).—I. The acid-catalysed anionotropic rearrangement reaction $\text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{C}\cdot\text{CH}$ (I) \rightarrow $\text{OH}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}\cdot\text{CH}$ (II) is of the first order (in 20% aq. EtOH) for (I) concns. ranging from 0.02 to 0.15 mol., the velocity coeff., k , decreasing slightly at higher (I) concn. k vals. were measured from the changes in absorption of ultra-violet light. (II) is formed to an extent $> 98\%$. k is \propto stoichiometric acid concn., C_A , when C_A is $< 0.1\text{M}$; at higher C_A vals. k becomes \propto Hammett's acidity function, (H_0). Catalysis was studied over the concn. range 0.02–4M. for HCl and 0.02–2M. for H_2SO_4 . An attempt was made to compare catalytic activity of different concns. of buffered solutions of AcOH of const. pH with catalytic activities of unbuffered AcOH solutions. Variation of k with the acid dissociation const., K_A , was studied for 8 acids used in 1M. concn., the K_A vals. ranging from 1.2×10^{-2} to 1.8×10^{-5} . The salt effect is positive and $\propto (H_0)$. Vals. of E over the temp. range 0 – 60° for different acids and acidities vary from 19,000 to 24,000. In 0.4M-HCl the vals. of k as measured from the change of optical rotation in a solution of a resolved sample of (I) ($[\alpha]_D^{20} + 45^\circ$) and that obtained from the light absorption changes are respectively $27.5 \pm 1.5 \times 10^4 \text{ min.}^{-1}$ and $32.8 \pm 0.6 \times 10^4 \text{ min.}^{-1}$. Reaction mechanism is interpreted in terms of a reversible oxonium ion formation, (I) + H^+ , accompanied by an irreversible electronic rearrangement, followed again by a reversible decomp. of the oxonium ion into (II) + H^+ the process being named "oxotropy."

II. Variation of k with change in the EtOH/ H_2O ratio (between 20 and 100% EtOH) has been studied over a wide range of HCl concns. (0.1–4M.) and of temp. (30 – 60°); the variation is also recorded for 0.2M- H_2SO_4 , M- H_3PO_4 , and M-AcOH, all at 60° , the changes in the EtOH/ H_2O ratio being between 0 and 100% EtOH in the case of AcOH. k decreases with increasing proportion of EtOH. For EtOH $\geq 80\%$ in HCl, the results are accurately represented by the equation $\log k = mD + n$, where D is dielectric const., m and n being const. for a given acid concn. and temp.; at EtOH $> 90\%$ k rapidly increases again. The equation does not apply in H_3PO_4 or AcOH when EtOH is $> 60\%$, and when 4M-HCl is used. The vals. of E (Arrhenius) range from 23,000 for 20% EtOH to 25,700 for 80% EtOH in the case of 0.1M-HCl; the corresponding vals. for 0.4M-HCl and M-HCl and for M-HCl (100% EtOH) are respectively 23,500 and 27,500; 24,200 and 26,500; and 22,500. The isodielectric energies of activation (energies of activation for a solvent of temp.-invariant dielectric const.) are added in the discussion of reaction mechanism. Experimental results are discussed in relation to work done by other investigators; the various modern concepts used point to rearrangement rather than to proton transfer as the rate-determining step.

J. L.E.

Influence of alkyl groups on reaction velocities in solution. V. Formation of phenyltrialkylammonium iodides in methyl alcohol. D. P. Evans (*J.C.S.*, 1944, 422–425).—Reaction rates of MeI with NPhMe_2 (I), NPhMeEt (II), NPhMeBu (III), and NPhBu_3 (VII) were found to be of the second order; those of MeI with NPhEt_2 (IV), NPhEtPr (V), and NPhPr_2 (VI) showed slight autocatalysis. Vals. of E for (I), (II), (III), (IV), (V), (VI), and (VII) are respectively: 15,200, 15,400, 15,430, 18,000, 19,030, 19,060, 19,000; those for $\log PZ$ are: 6.9, 6.9, 6.7, 7.7, 8.2, 8.1 and 8.1; the temp. ranges of reactions are: 25 – 65° , 45 – 84° , 45 – 84° , and 65 – 100° for the rest. The large increase in both the E and the $\log PZ$ vals. in passing from methylalkylanilines to higher alkylanilines is noteworthy; the possible causes of this effect are discussed, the likelihood of steric effect being emphasised. The comparison of dialkylaniline-MeI reaction velocities (in MeOH, at 65°) with those of dialkylaniline-allyl bromide (in EtOH, at 40°) shows that the variation in velocity from base to base is independent of the alkyl halide and is governed by the nature of the alkyl groups in the base; the velocity coeffs. of the two sets of reactions decrease in the order $\text{Me}_2 > \text{Me Et} > \text{Me Pr} > \text{Et}_2 > \text{Et Pr} > \text{Pr}_2$.

J. L.E.

Kinetics of aromatic sulphonation reactions. Sulphonation of *p*-nitrotoluene and of chlorobenzene by sulphur trioxide. K. D. Wadsworth and C. N. Hinshelwood (*J.C.S.*, 1944, 469–473; cf. A., 1939, I, 570).—The sulphonation reactions of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ (I) and of PhCl were found to be of the second order with respect to SO_3 , the velocity coeffs. being determined from the initial reaction rates at different SO_3 concns. Both reactions show strong retardation with time, being in this and other respects similar to the PhNO_2 sulphonation with SO_3 . The kinetic data for PhNO_2 (I), and PhCl sulphonations are respectively: $E = 11,400, 11,025$, and 7720 ; $\log PZ = 3.91, 4.79$, and 5.14 ; the probability factor $P = 1.9 \times 10^{-7}$, 1.65×10^{-6} , and 3.2×10^{-6} ; the temp. ranges of reactions were 25 – 100° , 0 – 60° , and 0 – 40° . The retardation of reactions

is ascribed to the formation of a complex $[\text{Ar}\cdot\text{SO}_3\text{H}\cdot\text{SO}_3]$; the second order may be due to 2 SO_2 mols. reacting either singly or as a dimer, S_2O_4 . The reactions were carried out in PhNO_2 ; the reaction rates were retarded by H_2SO_4 at low, but were little influenced at higher, temp. J. L.E.

Comparative study of the kinetics and mechanisms of formation of the phenylhydrazones, semicarbazone, and oxime of *d*-carvone. G. H. Stempel, jun., and G. S. Schaffel (*J. Amer. Chem. Soc.*, 1944, **66**, 1158—1161).—The reactions between NH_2OH , $\text{NHPh}\cdot\text{NH}_2$, and semicarbazide (I) and *d*-carvone proceed by the same mechanism, are acid-catalysed, show no salt effect, and have velocities \propto the concns. of the ketone and the carbonyl reagent. Data agree with Hammett's mechanism for the (I) reaction. W. R. A.

Velocity and yield in continuous reaction systems. K. G. Denbigh (*Trans. Faraday Soc.*, 1944, **40**, 352—373).—Two types of process are considered, one (tubular reactor) in which the reactants flow in uniform motion through a single vessel, with no mixing between different points on the line of flow, the second in which the reactants flow continuously through a series of tanks, in each of which a uniform concn. is maintained by stirring. The kinetics of processes of the latter type are often susceptible of much simpler mathematical treatment than are those of the former, since the evaluation of integrals is not involved. Equations giving the size of reaction space required for a given rate of output of reaction product are given. Where unwanted side reactions occur the tubular reactor gives the higher yield when the useful reaction is of higher order than the wasteful reaction, whilst in the opposite case the stirred tank reactor is to be preferred. In reversible consecutive reactions, the highest yield in a given time is obtained when the val. of some parameter, such as temp., is so adjusted that the reaction velocity is the max. possible at every moment. This principle is applicable to such processes as the catalytic oxidation of SO_2 and the synthesis of NH_3 , and the latter is given a detailed numerical treatment. F. L. U.

Analytical expressions of kinetic curves of phase transformations accounting for the dimensionality of growth of transformation products and the magnitude of three-dimensional nuclei. N. N. Sirota (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **36**, 175—179).—From Tamman's concept of a phase transformation as a process of creation of centres of new phases and the growth of these, kinetic expressions for phase transformations are deduced on the assumption that the transformations are isothermal and that the vol. of the mother phase remains const. Influence of the dimensionality of the growth of the centres of the transformation products and of the size of the three-dimensional nuclei is taken into account. For a small linear velocity of growth of the new phase (I) and a large velocity of the formation of centres, the magnitude of the three-dimensional nuclei must be considered. If the linear growth ceases the kinetics are similar to those of a first-order change. Except for the case of (I), the velocity coeff. is \propto the power of the time to the dimensionality of the growth. Variation of the probability of formation of two- and three-dimensional nuclei causes the exponent of the time to vary. The theory is briefly applied to a transformation of over-cooled austenite. J. O'M.B.

Mechanism of enzyme-inhibitor reactions.—See A., 1944, III, 766.

Velocity of tarnishing on metals as influenced by supersonic waves. J. A. Hedvall and G. Ekwall. **Supersonic wave apparatus.** K. Dahr (*Arkiv Kemi, Min., Geol.*, 1944, **18**, A, No. 11, 25 pp.).—The effect of supersonic waves on the tarnishing of Cu by I, and of Fe in O_2 at higher temp., has been investigated. In both cases the supersonic vibration resulted in a considerable increase in tarnishing velocity. The velocity of tarnishing was determined by optical interference methods. Local rise of temp. produced by the supersonic waves might be a contributory factor in the effect, but cannot completely account for it, as was shown by comparing the velocity of tarnishing of Fe at different temp. It is probably to be explained by enlargement of the reacting surfaces due to disturbances in the phase boundaries. The construction of the supersonic wave apparatus is fully detailed. A. J. M.

Catalytic decomposition of Tschugaev's pentammine $[(\text{NH}_3)_5\text{CIPt}]\text{Cl}_2$. A. M. Rubinshtein (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **28**, 55—58).—Solutions containing $[(\text{NH}_3)_5\text{CIPt}]\text{Cl}_2$ and $(\text{NH}_3)_4\text{PtCl}_2$ (I) at $>100^\circ$ ppt. a yellow salt having the composition $[(\text{NH}_3)_4\text{NH}_2\text{CIPt}]\text{Cl}_2 \cdot [(\text{NH}_3)_4\text{Cl}_2\text{Pt}]\text{Cl}_2$. The salt shows a single phase under the microscope, with monoaxial positive crystals; $N_m = 1.742$, $N_g > 1.790$. It is formed by catalytic decomp. of the pentammine at a rate which increases with the amount of (I) present; the latter remains unchanged in the solution, whilst the former is completely decomposed. L. J. J.

Free radicals in polymerisation processes. S. Medvedev, O. Koritzkaja, and E. Alexeeva (*J. Phys. Chem. Russ.*, 1943, **17**, 391—407).—When $\text{CH}_3\cdot\text{CCI}\cdot\text{CH}_2\cdot\text{CH}_3$ polymerises in vac. in presence of B_2O_3 or tetrahydronaphthalene hydroperoxide, the reaction mixture liberates I from HI in an amount $>$ that corresponding with the peroxide present, and also binds I in CHCl_3 ; the I-binding capacity is \propto the degree of polymerisation. This capacity is

attributed to the presence of free radicals, *i.e.*, long chains with non-saturated ends, in the mixture; a mutual saturation of these ends does not occur because of the high viscosity of the mixture. If to the mixture more of the monomer is added, it polymerises although no peroxide is present. If the polymer is recryst., it ceases to add I. If the polymerisation takes place in solution, the η of which is $<$ that of undiluted mixture, the mixture does not react with either HI or I. The simultaneous polymerisation of $(\text{CH}_2\cdot\text{CH})_2$ and $\text{CH}_2\cdot\text{CH}\cdot\text{CN}$ also forms free radicals. A theory of the rate of polymerisation is given; it assumes formation of free radicals and agrees with experiment. J. J. B.

Antioxidant properties of *d*-isoascorbic acid and its sodium salt.—See A., 1944, III, 825.

Temperature activation and inactivation of the crystalline catalase-hydrogen peroxide system.—See A., 1944, III, 839.

Apparent heats of activation and surface activity in surface catalysis over wide ranges of temperatures. F. H. Constable (*Rev. Fac. Sci. Istanbul*, 1943, **8**, A, 112—119).—Mathematical. An equation for the apparent heat of activation is derived, and the significance of one of the terms in the equation being negative, zero, or positive is discussed. This term is $(1/h) - 1/RT$, where h is the const. occurring in the author's equation connecting the no. of active centres in a catalyst surface with the heat of activation on each centre and which depends on surface conditions. C. R. H.

Kinetics of ammonia decomposition on iron catalysts. I. Chrisman and G. Korneitschuk (*Acta Physicochim. U.R.S.S.*, 1943, **18**, 420—429).—Discrepancies observed in data on the kinetics of NH_3 decomp. on Fe catalysts are due to structural differences in the catalyst. If a const. catalytic surface is maintained, reproducible results can be obtained. On a promoted technical Fe catalyst of the type $\text{Fe}-\text{Al}_2\text{O}_3-\text{K}_2\text{O}$ free from nitride the decomp. of NH_3 is ~ 100 times as fast as on promoted nitride of the type $\text{Fe}_3\text{N}-\text{Al}_2\text{O}_3-\text{K}_2\text{O}$. C. R. H.

Dendrite hypothesis of carbon deposition. Chemical behaviour of cyclohexane when in contact with electrically heated metallic coils. A. Balandin and N. Kotelnikov (*Acta Physicochim. U.R.S.S.*, 1943, **18**, 406—419).—The catalytic dehydrogenation and decomp. of cyclohexane over Pt- and Pd-nichrome, nichrome, Cr-Fe, and Fe at $300-600^\circ$ has been investigated. Nichrome, Cr-Fe, and Fe are inactive. Pd-nichrome is a poor catalyst. Pt-nichrome is a good catalyst at higher temp. The deposition of C does not diminish the dehydrogenation activity of the catalyst; on the contrary, the activity is increased. Deposition of C in the form of dendrites is suggested in explanation. C. R. H.

Formation of carbon dendrites by catalytic decomposition of alcohols on metals. A. A. Balandin and V. V. Patrikeev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **40**, 152—154).—The catalytic decomp. of Pr°OH on a constantan wire leads to deposition of C in the form of dendrites. It is possible that a film of carbide is first formed on the metal which is subsequently decomposed to C and metal, the latter being in a looser form than originally. The dendrites start growing from the deposited metal crystals. This behaviour is not observed in similar experiments with cyclohexane. The dendrites contain O and H corresponding with $\text{C}_{22}\text{H}_4\text{O}$. Calculation of the diameter of a crystallite gives $d = 45 \text{ \AA}$, a val. intermediate between the vals. calc. for peat coke and C_2H_2 soot. C. R. H.

Catalysis in producing potassium and sodium sulphates from chlorides decomposed with sulphur dioxide in the presence of oxygen. S. I. Volkovitsch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **41**, 21—23).—The oxidation of SO_2 to SO_3 in the vapour phase in presence of H_2O (for conversion of KCl into K_2SO_4 with SO_2 in presence of O_2 at $500-550^\circ$) can be accelerated several hundred times by means of catalysts containing Fe_2O_3 . Burnt pyrites refuse from H_2SO_4 manufacture is best used as a 1% admixture by wt. with the KCl . 90—95% recovery of K_2SO_4 is obtained with a reaction time of >1.5 hr. and 40% utilisation of the SO_2 per passage. L. J. J.

Catalytic alkylation of hydrocarbons in the gas phase. G. L. Natanson and M. J. Kagan (*J. Phys. Chem. Russ.*, 1943, **17**, 381—390).—Synthetic aluminosilicates are catalysts at $400-430^\circ$ for the reactions $\text{C}_6\text{H}_6 + \text{C}_2\text{H}_4 \rightarrow \text{PhEt}$ (yield, *e.g.*, 17% of the C_6H_6 employed), $\text{PhEt} \rightarrow \text{C}_6\text{H}_6 + \text{C}_2\text{H}_4$ (yield, *e.g.*, 25%), and $\text{PhMe} \rightarrow \text{C}_6\text{H}_6 + \text{C}_2\text{H}_5\text{Me}$ (yield, *e.g.*, 15%). The mechanism of these reactions is discussed. J. J. B.

Preparation and reclamation of copper-chromium oxide catalyst [for the dehydrogenation of alcohols]. R. E. Dunbar and M. R. Arnold (*Ind. Eng. Chem. [Anal.]*, 1944, **16**, 441).—Celite Carrier Type VII (I) and Carborundum Brand porous aggregates are satisfactory new inert carriers for supporting this catalyst. (I) is a porous variety of pellets possessing greater mechanical strength than the granular Celite previously used. The customary AcOH leaching and washing of the catalyst can be substituted by careful heating in air at 150° . $\text{Cu}-\text{Cr}_2\text{O}_3$ catalyst that has become sluggish in action from prolonged use can be reactivated by heating to expel absorbed org. matter and to reoxidise the metals. Leaching with AcOH and washing then provides a catalyst as active as the original.

Data showing the behaviour of six Cu—Cr₂O₃ catalysts supported on three inert materials are recorded for the dehydrogenation of Bu^oOH. L. S. T.

Magnetic studies of chromium oxide catalysts.—See A., 1944, I, 272.

Catalytic aromatisation of branched chain aliphatic hydrocarbons.—See A., 1944, II, 357.

Action of chromia catalyst on aliphatic iso-alcohols.—See A., 1944, II, 357.

Catalytic vapour-phase oxidation of nicotine to nicotinonitrile.—See B., 1944, II, 301.

Chemical-catalytic liquid-phase oxidation of nicotine, β -picoline, and quinoline to nicotinic acid.—See B., 1944, I, 302.

Mechanism of electrolytic oxidation of aluminium. S. Anderson (*J. Appl. Physics*, 1944, 15, 477—480).—It is suggested that in anodic Al₂O₃ films on Al, the porous film of Al₂O₃ is separated from the Al surface by a compact barrier layer of Al₂O₃ which is continuous, unbroken, and the seat of growth processes from which the porous coating originates. The barrier layer is formed by diffusion of Al⁺⁺⁺ ions to the solution without remaining in the film. Electric conduction within the film allows O[—] ions to pass O[—] through spaces left by diffusion of Al⁺⁺⁺ ions through it. The theory accounts for the adherence, porosity, experimental "efficiency ratios," and luminescence. L. J. J.

Structure of anodic coatings [on aluminium].—See B., 1944, I, 373.

Electrodeposition of brass.—See B., 1944, I, 373.

Electrochemical oxidation of *n*-butyl alcohol. II. I. I. Radtschenko (*J. Appl. Chem. Russ.*, 1940, 13, 1348—1354).—A solution of Bu^oOH in 4% H₂SO₄, or a two-phase mixture of these liquids, was oxidised at a Pb anode. When the ratio [Bu^oOH] : [H₂SO₄] increased from 0.04 to 0.53 the yield of Pr^oCO₂H decreased from 23—42% to 4—6% and the yield of PrCO₂Bu (I) rose from 18—42% to 40—52%. The effect of the c.d. (0.01—0.06 amp. per sq. cm.) on these yields was less definite. The yield of CO₂ increased with c.d. The formation of (I) takes place probably at the line between the H₂SO₄ layer, the Bu^oOH layer, and anode, where the [H₂SO₄] is very high. J. J. B.

Mechanism of formation and development of a latent photographic image. P. D. Dankov and A. A. Kotschetkov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 785—787).—The theory previously put forward (A., 1940, I, 124) requires for its verification the presence of orientational relations between crystals of AgBr and those of Ag. Evidence of this has now been obtained. Monocryst. films of AgBr were pricked with a blunt needle. Crystal deformation lines appeared in the form of rosettes. At liquid air temp. instead of rosettes, cracks were formed along the cleavage planes. The crystals were then developed. Ag crystals were formed, strictly oriented both in relation to the deformation figures obtained before development, and with regard to each other. When the AgBr was deformed at liquid air temp. the Ag crystals developed so that the [110] axis of the Ag coincided with the [010] axis of the AgBr. When a monocryst. AgBr film was partly reduced (1 min. in developer) the film was covered with very small regular crystals of Ag, but each crystal had a thin sinuous continuation. With further reduction the small crystals grow together and completely cover the surface. A. J. M.

Kinetics and mechanism of photographic development. I. Kinetics of development of single grains.—See B., 1944, II, 337.

Photochemical investigation of dark-coloured aniline. A. T. Vartanjan (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 635—638).—Pure NH₂Ph kept in a high vac. (10^{−5} mm.) did not become discoloured on keeping in the dark or on exposure to diffuse daylight. It rapidly became coloured when exposed to Mg sparks filtered through Iceland spar or gelatin. Light of $\lambda \geq 2800$ Å. is effective. Increase of temp. causes a considerable increase in the velocity of the photochemical reaction, and the walls of the vessel become covered with resinous products, consisting of a volatile and a non-volatile portion. H₂ and NH₃ are also formed. C₆H₆ could not be detected spectrographically owing to the extinction effect of NH₂Ph. Excitation of the vapour in a quartz vessel gives rise to a yellowish-green fluorescence with a continuous spectrum over the range 6300—3840 Å. The carrier of the fluorescence is probably azophenine. The primary processes are the splitting off of NH₂ and H from the Ph radical, as is shown by the analysis of the absorption spectrum of NH₂Ph. The reactions are: NH₂Ph + $h\nu$ → NHPh + H; NH₂Ph + $h\nu$ → C₆H₄NH₂ + H; NH₂Ph + $h\nu$ → Ph + NH₂. The radicals C₆H₄NH₂, NHPh, and C₆H₄NH lead to the formation of azophenine. Increase of temp. causes a displacement of the predissociation limit and the continuous absorption towards longer λ . A. J. M.

Asymmetric photolysis of β -chloro- β -nitroso- α -diphenylbutane with circularly polarised light. S. Mitchell and I. M. Dawson (*J.C.S.*, 1944, 462—454; cf. A., 1941, II, 349).—A resolution of the racemic

form of a chloronitroso-compound was accomplished using the phenomenon of "circular dichroism" which is of interest in connexion with the origin of optically active compounds in nature. CH₂Ph·CCl(NO)·[CH₂]₂·Ph selected for photolysis satisfies the three photochemical requirements: (a) the main product of photolysis (in MeOH), CH₂Ph·C(N·OH)·[CH₂]₂·Ph·HCl, contains no asymmetric C atom; (b) sufficiently high quantum efficiencies—these being per λ 6100 and 6580 Å., 1.10 and 0.78, respectively, with the average of 0.94; (c) the absence of dark reaction. The progress of the photolysis was followed by means of a photoelectric colorimeter, the first stage of the decomp. being carried to the extent of 50%, while in each of the three subsequent stages 40% of the recovered compound was decomposed; the total decomp. was equal to 90% of the original material. The final specimen of the compound exposed to the right-handed light gave the polarimetric val. $\alpha_{5500} = -0.10^\circ$, and the specimen exposed to the left-handed light gave $\alpha_{5500} = +0.11^\circ$ ($l = 1$, $c = 4\%$, in MeOH). J. L. E.

Photochemical properties of 1 : 4-dimethoxy-9 : 10-diphenylanthracene. R. Audubert and C. Racz (*Compt. rend.*, 1943, 216, 413—414).—The threshold frequency for the photochemical reaction $R + O_2 \rightarrow RO_2$ has been determined for 1 : 4-dimethoxy-9 : 10-diphenylanthracene (0.018 g. per l.) dissolved in anhyd. Et₂O. The oxidation reaction was followed photometrically. The threshold is 4550 Å. (61,060 g.-cal.), giving 85,000 g.-cal. as an upper limit for the heat of dissociation of the oxide (energy of activation 24,000 g.-cal.). Hence mol. O₂ is liberated in the dissociation. L. J. J.

IX.—PREPARATION OF INORGANIC SUBSTANCES.

Reactions in the solid state. P. P. Budnikov and A. S. Bereshnoi (*J. Appl. Chem. Russ.*, 1940, 13, 1277—1287).—A review of recent German publications. J. J. B.

Complex compounds of cupric azide. III. Non-electrolytes with organic bases. A. Cirulis and M. Straumanis (*J. pr. Chem.*, 1943, [ii], 162, 307—328).—The following compounds of general formula [Cu(amine)₂(N₃)₂] are prepared (a) from Cu(N₃)₂ (cf. Cirulis, A., 1939, I, 621) and the amine in boiling EtOH, or (b) from Cu(NO₃)₂ in MeOH, the amine, and NaN₃ (methods of prep. indicated in parentheses): *bis*-allylamine- (a, b), decomp. 179—180°, *benzylamine*- [a, b], or from benzylamine azide and Cu(N₃)₂ in H₂O at the b.p., m.p. 152°, *tetrahydro- β -naphthylamine*- (b), m.p. 115°, *bornylamine*- (b), decomp. 207—208°, *β -picoline*- (I) (a, b), explodes 207—215° (preheated block) or on strong percussion, *2 : 6-dimethylpyridine*- (b), explodes 202—203°, *2 : 4 : 6-trimethylpyridine*- (b), explodes 198—202° (slow heating) or 220—225° (preheated block), *piperidine*- (a), m.p. 109°, *cyclohexylamine*- (b), m.p. 134°, *2-aminotriazole*- (b), decomp. 145—150°, *isouquinoline*- (b), decomp. 197—200°, *6-* (b), decomp. 210—213°, and *7-methylquinoline-diazidocopper* (b), decomp. 138—140°. Compounds of formula [Cu(amine)(N₃)₂] are prepared similarly: *o*-, *m*-, and *p*-toluidine- (b), explode 123°, 157—160°, and 135° respectively, *o*-anisidine- (b), detonates 125° (preheated block), "1 : 4 : 5-" (b), explodes 130° (preheated block), and "1 : 3 : 4-" *xylydine*- (b), decomp. 106—108°, *ψ -cumidine*- (b), m.p. 119° (decomp. 120°), *benzidine*- (b), amorphous, *o*-tolidine- (b), decomp. unsharply, *o*-diamisidine- (b), decomp. 122—124°, *p*-nitrosodimethylamine- (b), ignites 132°, *a*-picoline- (a, b), detonates 204—205°, *β -picoline*- [a, or from (I) in hot MeOH], explodes 210—211°, *2 : 4-dimethylpyridine*- (b), explodes 208—209°, *quinoline*- (a, b), explodes 207—208°, *piperazine*- (b), decomp. 150°, *benzimidazole*- (b), decomp. 183—185°, and *nicotine-diazidocopper* (a, b), m.p. 108°. Compounds of the formula [Cu(N₃)₂(amine)Cu(N₃)₂] are also prepared similarly: *hexamethylene-tetramine*- (b), explodes 180—185° or on strong percussion, *quinine*- (b) (+3H₂O), explodes 149—151°, *quinidine*- (b), explodes 152—154°, *cinchonine*- (b), decomp. 154—155°, *cinchonidine*- (b), inflames 169°, and *brucine-tetra-azidocopper* (b), decomp. 145—147°. *Bis-triethanolaminediazido-oxocopper*, [Cu₂N₃]₂O(C₆H₅O₃N)₂ (b), m.p. 172°, is also prepared. The above compounds are green or brownish, insol. in and stable to cold H₂O, decomp. in hot H₂O; in most, Cu has co-ordination no. 3. The compounds marked * explode on percussion. E. W. W.

Magnesium and barium beryllates. (Mlle.) M. L. Quinet (*Compt. rend.*, 1943, 216, 297—299).—Addition of a Mg salt in aq. solution to an alkaline Be(OH)₂ solution gives a ppt. containing Mg₃BeO₄·*n*H₂O. No Mg can be detected in the solution. A similar reaction is found with Ba—Be solutions >1 or <0.1N. in alkali. With intermediate alkali concns., the solution contains Ba and Be in equimol. ratio. BaBeO₄ is also found in the ppt. and solution when Be(OH)₂ is added to Ba(OH)₂ solutions. L. J. J.

Precipitation of mercury from solutions of sulphides with amalgamated zinc. I. N. Plaksin and L. D. Plaksina (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 40, 188—190).—Zn amalgam containing 4% of Hg ppts. up to 98.5% of Hg from Na₂S solutions in 12 hr. With a higher Hg : Zn ratio 99.9% of the Hg can be pptd. in 30 min. The temp. range 9—20° is suitable. Pptn. of Hg from BaS solutions

with amalgamated Zn requires temp. $<10^\circ$ and alkalinity $<0.5\%$. The consumption of Zn is 1.5—2 times the wt. of Hg recovered.

L. J. J.

Etching figures on the surfaces of aluminium crystals. II. H. Mahl and I. N. Stranski (*Z. physikal. Chem.*, 1942, B, 52, 267—262).—Etching of Al crystals with aq. or alcoholic HCl shows a cubic structure. If the etching is done by dry HCl at high temp., octahedra in combination with cubes are observed. This is in agreement with the theory that in the case of aq. and alcoholic HCl the etching figures are due to dissolution of a reaction product, whereas with dry HCl at the temp. used any AlCl_3 produced would be volatilised off.

A. J. M.

Aluminium orthohydroxide and its transformation into bayerite. H. Kraut, E. Flake, W. Schmidt, and H. Volmer (*Ber.*, 1942, 75, [3], 1357—1373).— $\text{Al}(\text{OH})_3\text{-C}_a$ is obtained by the action of aq. NH_3 on $\text{Al}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$ and filtration of the ppt., which is agitated with successive amounts of H_2O over long intervals of time; the pH of the solution must be >7.4 . The product usually contains SO_4^{2-} , which can be removed only by very careful, prolonged washing. Such preps. are very rapidly sol. in 0.1% HCl but this property, which is very sensitive to pH, is immediately lost if pH reaches 8. The ageing of $\text{Al}(\text{OH})_3\text{-C}_a$ is followed by periodical determinations of H_2O and Debye-Scherrer X-radiograms, those of bohmite in its different stages of formation, bayerite-A, -B, and -C, and hydrargillite being determined for comparison. C_a shows no interferences. Products undergoing ageing show the bohmite lines until the min. H_2O content is reached (poly-Al hydroxide-A gives well defined bohmite lines). The rate of alteration varies greatly with the details of prep. and, particularly, with the $[\text{NH}_3]$ in the ultimate suspension. Further ageing causes the bayerite lines also to appear, with gradually increasing intensity, until they alone are observed. The H_2O content gradually increases. The hitherto unknown lattice of bayerite-C (prep. described) appears only when ageing of C_a occurs under NH_3 .

H. W.

Basic lanthanum nitrite. G. R. Sherwood (*J. Amer. Chem. Soc.*, 1944, 66, 1228—1229).—*La basic nitrite*, prepared from LaCl_3 or $\text{La}(\text{NO}_3)_3$ by the method of Sherwood and Hopkins (A., 1933, 1008), liberated I from HI, reduced acidified KMnO_4 , and was thermostable up to the b.p. of conc. H_2SO_4 . The speed of pptn. increased with $[\text{NO}_2^-]$ and ppts. obtained using different initial $[\text{NO}_2^-]$ (0.5—2.0M.) gave identical analyses. With $[\text{NO}_2^-] < 0.5\text{M.}$ no nitrite was obtained; presumably only $\text{La}(\text{OH})_3$ was pptd. To prevent formation of colloidal particles the $\text{La}(\text{NO}_3)_3$ should have an initial pH ~ 5 .

W. R. A.

Artificial production of diamonds. C. H. Desch (*Nature*, 1943, 152, 148—149).—The conclusion that diamonds have not been prepared artificially is reviewed in the light of recent X-ray investigations of Hannay's artificial crystals.

E. R. R.

Pure charcoal from cane sugar.—See B., 1944, I, 354.

Preparation of silicon tetrachloride and its use as a basis for obtaining silicic acid esters. K. Andrianov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 66—69).—Ferrosilicon containing 35—65% Si reacts with dry Cl_2 at temp. $>200^\circ$. The reaction is thermally self-supporting. As by-products, FeCl_3 is formed in negligible amounts, and SiCl_4 to the extent of 3—10% of the SiCl_4 at temp. $<450^\circ$. No Si_2Cl_6 is formed above 450° . The yield of SiCl_4 reaches a max. val. of $\sim 95\%$ at 600° . Esters of $\text{Si}(\text{OH})_4$ are prepared by adding SiCl_4 dropwise to the alcohol at 0° , stirring for 1 hr. at room temp., and heating at $80\text{—}90^\circ$ for 2 hr. The best yield is obtained with $>10\%$ excess of alcohol. Insufficient proportions of alcohol give some Cl-ester. The yield is adversely affected by the presence of H_2O in the alcohol. 70—84% yields are quoted for Me, Et, and Bu esters.

L. J. J.

Separation of oxygen isotopes by distillation of water. H. G. Thode, S. R. Smith, and F. O. Walkling (*Canad. J. Res.*, 1944, 22, B, 127—136).—The apparatus consists of three 25-ft. columns of decreasing diameter arranged in cascade (A., 1939, I, 211). Mounting is staggered to facilitate pumping between shafts. Haydrite aggregate is a suitable packing material and could be used in the tubes of 2—3 ft. diameter. Only 15% of the liquid held drains immediately from such a packing; hence the columns can be closed for repair without complete mixing of all the column materials. The accuracy of the spectrographic examination of ^{18}O was $>1\%$. Analysis of H_2^{17}O was direct owing to coincidence of the mass spectrographic lines of $^{13}\text{C}^{16}\text{O}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}^{17}\text{O}$. Distillation for 120 days produced 23 g. of ^{18}O in excess of normal, including 150 ml. of water enriched 6.5-fold in ^{18}O and 2.7-fold in ^{17}O . The v.p. of the H_2^{17}O is the algebraic or geometric mean of the v.p. of H_2^{16}O and H_2^{18}O . Cohen's theory for the operation of packed fractionating columns explains the effect of rate of flow on equilibrium fractionation and agrees qualitatively with the production rates of ^{18}O . The 50% efficiency obtained is the same as that reported by Cohen in the chemical exchange process: $(\text{NaCN}_{\text{sol}}\text{-HCN}_{\text{gas}})$.

J. O'M-B.

Oxidation of hydrogen sulphide by chromates in aqueous solution or suspension. H. B. Dunncliff (*J. Indian Chem. Soc., Ind. Ed.*,

1944, 7, 43—46).—A review.

Full scheme of the reactions occurring is given. M. H. M. A.

Lower oxides of sulphur. I, II. P. W. Schenk (*Chem.-Ztg.*, 1943, 67, 251—253, 273—276).—A review of published information on the prep., purification, and properties of SO , poly-S oxides, and S_2O_5 .

L. J. J.

Normal and poly-molybdates of some complex cations and the composition and constitution of metamolybdates. P. Rây and B. Sarma (*J. Indian Chem. Soc.*, 1944, 21, 139—144).—The prep. of the following is described: $[\text{CoX}_3]\text{ClMoO}_4$, $[\text{CoX}_3]_2[\text{MoO}_4]_3 \cdot 6.5\text{H}_2\text{O}$, $[\text{CoX}_3]_2[\text{MoO}_4]_3 \cdot 3\text{H}_2\text{O}$, $[\text{NiX}_2]_2[\text{MoO}_4]_3 \cdot 3\text{H}_2\text{O}$, $[\text{CuX}_2]_2[\text{MoO}_4]_3 \cdot 2.5\text{H}_2\text{O}$, $[\text{CoX}_3]_2[\text{MoO}_4]_3 \cdot 9\text{H}_2\text{O}$, $[\text{CoX}_3]_2[\text{HMoO}_4]_3 \cdot 12.5\text{H}_2\text{O}$ (I), $[\text{Co en}]_2[\text{HMoO}_4]_3 \cdot 13.5\text{H}_2\text{O}$ (II), and $[\text{Co en}]_2[\text{HMoO}_4]_3 \cdot 11.5\text{H}_2\text{O}$ (III), where X = biguanide and en = $(\text{CH}_2\text{NH}_2)_2$. (I), (II), and (III) lose their H_2O of crystallisation at 100° , leaving three mols. of combined H_2O . This is regarded as evidence in favour of Rosenheim's structure for the metamolybdates, which are represented by $\text{R}_6\text{H}_4(\text{Mo}_2\text{O}_7)_3 \cdot \text{aq.}$

C. R. H.

Synthesis of ammonium phosphates from ferroferriphosphates. M. M. Bikov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 40, 66—69).—The compound $\text{FeO}_4\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 21\text{H}_2\text{O}$ has been obtained by natural oxidation (10 years) of Fe^{II} phosphate; oxidation of this or of natural β -kerchenite at 600° gives the compound $3\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5$. Crystal-optical data are given for these and $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. Fe phosphates may be converted into NH_4 phosphates by $(\text{NH}_4)_2\text{S}$.

W. R. A.

Nickelocyanic acid and its salts. F. Feigl, V. Demant, and O. E. de Oliveira (*Anais Assoc. Quim. Brasil*, 1944, 3, 72—87).— $\text{K}_2[\text{Ni}(\text{CN})_4]$ with CuSO_4 gives $\text{Cu}[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$, which with aq. NH_3 yields $[\text{Cu}(\text{NH}_3)_4][\text{Ni}(\text{CN})_4]$. $\text{Co}[\text{Ni}(\text{CN})_4]$, $\text{UO}_2[\text{Ni}(\text{CN})_4]$, $\text{Mn}[\text{Ni}(\text{CN})_4]$, $\text{Fe}[\text{Ni}(\text{CN})_4]$, $[\text{Fe}^{II}(\text{C}_5\text{H}_4\text{N})_2][\text{Ni}(\text{CN})_4]$ and $(\text{pp-NH}_2 \cdot \text{C}_6\text{H}_4)_2\text{H}_2[\text{Ni}(\text{CN})_4]$ were also prepared. The compound of Bernoulli and Grether (A., 1901, i, 584) from $\text{Ni}(\text{CN})_2$ and NH_3 is also obtainable from $[\text{Ni}(\text{NH}_3)_4]\text{Cl}_2$ and $\text{K}_2[\text{Ni}(\text{CN})_4]$ but is considered to be a mixture of $[\text{Ni}(\text{NH}_3)_4][\text{Ni}(\text{CN})_4]$ and $[\text{Ni}(\text{NH}_3)_2][\text{Ni}(\text{CN})_4]$. For a compound described by Hofmann and Küspert (A., 1897, i, 546) the formula $[\text{Ni}(\text{NH}_3)_2(\text{C}_5\text{H}_4\text{N})_2][\text{Ni}(\text{CN})_4]$ is proposed. $\text{Ni}(\text{CN})_2$ is considered to be $\text{Ni}[\text{Ni}(\text{CN})_4]$ because with $(\text{CH}_3\text{NH}_2)_2$ (en) it gives $[\text{Ni en}]_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$. $[\text{Ni}(\text{NH}_3)_4][\text{Ni}(\text{CN})_4]$, $[\text{Ni}(\text{C}_5\text{H}_4\text{N})_2][\text{Ni}(\text{CN})_4]$, and probably $[\text{Ni}(\text{C}_5\text{H}_4\text{N})_2][\text{Ni}(\text{CN})_4]$ were also prepared. $\text{K}_2[\text{Zn}(\text{CN})_4]$ with NiSO_4 gives $\text{Ni}[\text{Zn}(\text{CN})_4]$ which in aq. suspension at 90° is converted into $\text{Zn}[\text{Ni}(\text{CN})_4]$, also obtained from $\text{K}_2[\text{Ni}(\text{CN})_4]$ with ZnSO_4 , $\text{Ni}(\text{CN})_2$ with $\text{Zn}(\text{CN})_2$, $\text{Ni}(\text{CN})_2$ with $\text{Zn}(\text{NO}_3)_2$, and $\text{Zn}(\text{CN})_2$ with $\text{Ni}(\text{NO}_3)_2$. $\text{Cd}[\text{Ni}(\text{CN})_4]$ is obtained by analogous methods even in the cold.

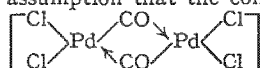
F. R. G.

Pyridine complexes of rhodous halides.—See A., 1944, II, 377.

Thiosulphate compounds of palladium. D. I. Riabtschikov and A. P. Isakova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 161—164).—When acted on by $\text{S}_2\text{O}_3^{2-}$, Pd salts react in an analogous manner to those of Pt. Equimol. quantities of $\text{K}_2[\text{PdCl}_4]$ (I) and $\text{Na}_2\text{S}_2\text{O}_3$ react to form a black ppt. of $\text{PdS}_2\text{O}_3 + \text{PdS}$. Pptn. of Pd is quant. With <2 mols. of $\text{Na}_2\text{S}_2\text{O}_3$, yellow $\text{K}_2[\text{Pd}(\text{S}_2\text{O}_3)_2]$, sol. in an excess of $\text{Na}_2\text{S}_2\text{O}_3$, is pptd. $[\text{PdCl}_4][\text{Pd}4\text{NH}_3]$ dissolves readily in aq. $\text{Na}_2\text{S}_2\text{O}_3$ at the ordinary temp. to yield an orange-coloured solution from which EtOH ppts. bright yellow $[\text{Pd}(\text{S}_2\text{O}_3)_4][\text{Pd}4\text{NH}_3]$. Aq. *trans*- $[\text{Pd}2\text{NH}_3\text{Cl}_2]$ and aq. $\text{Na}_2\text{S}_2\text{O}_3$ form sparingly-sol., pale yellow $[\text{Pd}2\text{NH}_3\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}]$. With aq. $\text{Na}_2\text{S}_2\text{O}_3$ and aq. $[\text{Pd}4\text{NH}_3]\text{Cl}_2$ the reactions $[\text{Pd}4\text{NH}_3]\text{Cl}_2 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow [\text{Pd}4\text{NH}_3]\text{S}_2\text{O}_3 + 2\text{NaCl}$, or $[\text{Pd}3\text{NH}_3\text{S}_2\text{O}_3] + 2\text{NaCl} + \text{NH}_3$, or $[\text{Pd}2\text{NH}_3\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}] + 2\text{NaCl} + 2\text{NH}_3$, can take place. With 2 mols. of $\text{Na}_2\text{S}_2\text{O}_3$, the reaction $[\text{Pd}4\text{NH}_3]\text{Cl}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2[\text{Pd}2\text{NH}_3(\text{S}_2\text{O}_3)_2] + 2\text{NaCl} + 2\text{NH}_3$ occurs. The $\text{CS}(\text{NH}_2)_2$ derivative $[\text{Pd}4\text{CS}(\text{NH}_2)_2]\text{Cl}_2$ and $\text{Na}_2\text{S}_2\text{O}_3$ in conc. solution yield an orange-red ppt. of $(\text{Pd}2\text{CS}(\text{NH}_2)_2 \cdot \text{S}_2\text{O}_3 \cdot \text{H}_2\text{O})$ with $\text{CS}(\text{NH}_2)_2$ in the *trans*-position. With an excess of $\text{Na}_2\text{S}_2\text{O}_3$, the sol. product is $\text{Na}_2[\text{Pd}2\text{CS}(\text{NH}_2)_2 \cdot 2\text{S}_2\text{O}_3]$, which crystallises with 6 H_2O on treatment with EtOH and evaporation over H_2SO_4 in an atm. of CO_2 . The $(\text{CH}_3\text{NH}_2)_2$ (en) compound $[\text{Pd}2\text{ en}]\text{Cl}_2$, prepared by heating (I) with an excess of $(\text{CH}_3\text{NH}_2)_2$, reacts with $\text{Na}_2\text{S}_2\text{O}_3$ to give $[\text{Pd enS}_2\text{O}_3]$ and $\text{Na}_2[\text{Pd en}(\text{S}_2\text{O}_3)_2]$. Excess of $\text{Na}_2\text{S}_2\text{O}_3$ displaces en completely from the inner sphere, $\text{S}_2\text{O}_3^{2-}$ residues being substituted.

L. S. T.

Compounds of palladium with carbon monoxide. A. Gelman and E. Meilach (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 171—174).—By passage of CO for several days through $(\text{NH}_4)_2\text{PdCl}_4$ in conc. HCl the compound obtained is not $\text{NH}_4[\text{PdCl}_3\text{CO}]$ but $\text{NH}_4[\text{PdCl}_4\text{CO}]$. By metathesis reactions with $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ and with $(\text{CH}_3\text{NH}_2 \cdot \text{HCl})_2$ the compounds $[\text{Pt}(\text{NH}_3)_4][\text{PdCl}_4\text{CO}]_2$ and $(\text{enH}_2)[\text{PdCl}_4\text{CO}]_2$ have been isolated. The structure of these compounds is discussed in terms of the co-ordination theory, and formulæ are advanced on the assumption that the compounds are dimerides containing the ion



The instability of the Pd carbonyl halides probably causes Pd to be tervalent in these compounds.

J. O'M-B.

X.—LECTURE EXPERIMENTS AND HISTORICAL.

Founders of the Italian school of chemistry. D. Marotta (*Ber.*, 1942, 75, [B], 2095—2100).—An historical review dealing with the work of Piria, Cannizzaro, and Paterno. It is claimed that Paterno originated the hypothesis of the tetrahedral C atom. A. J. M.

William Albert Noyes. B. S. Hopkins (*J. Amer. Chem. Soc.*, 1944, 66, 1045—1056).—Obituary notice. W. R. A.

XI.—GEOCHEMISTRY:

Chemistry of the earth. J. S. Anderson (*J. Proc. Roy. Soc. New South Wales*, 1943, 76, 329—344).—A lecture. Recent contributions of geochemistry to the problems of the relative and absolute abundance of the elements and their distribution are reviewed. C. R. H.

α -Helium method for determining geological ages. R. D. Evans and C. Goodman (*Physical Rev.*, 1944, [ii], 65, 216—227).—New techniques for determining the rate of He production in igneous rocks by direct counting of the α -rays and the removal and measurement of He accumulated in rock during geologic time provide a direct, simple, and rapid physical method of He age analysis. Equations are derived relating the true rate of He production to the observed rate of α -particle emission from a thin source. Simple, accurate age corrections to the approximate age are derived. Agreement between " α -He" and "Rd-Tn-He" ages on the same samples indicates that the accepted decay constants of the parent elements, Th and U, are correct to ± 5 –10%. Certain mineral constituents allow a significant amount of their radiogenic He to escape during geologic time. Magnetite is a suitable retentive mineral to serve as a basis for the revised He scale. The α -activity of 81 rock specimens ranges from 0 to 5.8 with an average of 1.23 α -rays per hr. per mg. N. M. B.

Helium content of air. E. Gluckauf (*Trans. Faraday Soc.*, 1944, 40, 436—439).—A simple method is described in which He in air is determined with an accuracy of 1% by treatment with C cooled in liquid N₂ until all the Ne and part of the He has been absorbed. The residual He is measured, and the amount found is corr. for the absorbed fraction by means of a duplicate experiment with He-free air containing a measured quantity of He, carried out under identical conditions. The val. found is 5.24 ± 0.03 p.p.m. by vol., in good agreement with more exact determinations. F. L. U.

Hydrology of the Sierre (Valais) region. I. Relation between superficial and deep waters. II. G ronde lakes. J. P. Buffle (*Arch. Sci. phys. nat.*, 1943, [v], 25, Suppl., 286—292, 292—295).—I. Chemical analyses of the H₂O of the Rhone, the sources of the G ronde lake, and various well waters are recorded and discussed.

II. Chemical analyses of the waters of the Rhone, and of the large and the small lakes of G ronde, are recorded. The lack of any direct relationship between the large G ronde lake and the Rhone is confirmed. The big difference in composition between the H₂O of the large G ronde lake and that of the H₂O of the small lakes east and west of it is discussed. L. S. T.

Source of supply of Blue lake near Kandersteg (Bernese Oberland). P. Buffle (*Arch. Sci. phys. nat.*, 1944, [v], 26, Suppl., 18—22).—Chemical analyses of the lake H₂O and the H₂O of the River Kander are recorded. Comparison of the data excludes direct communication between the two, but the possibility of indirect communication is discussed. L. S. T.

Sodium sulphate waters of the Kungurian deposits at Levshino. A. M. Kuznetsov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 424—427).—Analytical data on waters drawn from wells bored in different rocks to different depths are discussed and explanations of the base-exchange and other processes responsible for their formation are advanced. W. R. A.

Boron contents of some lakes of Western Kazakhstan. D. I. Kuznetsov (*J. Appl. Chem. Russ.*, 1940, 13, 1332—1335).—KCl and B₂O₃ contents of 50 H₂O samples are given; the highest [B₂O₃] was 0.053%. J. J. B.

Manganese in the sediments of polar seas. M. V. Klenova and A. S. Pachomova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 87—89).—The Mn content of mud samples from the Barentz, Kara, and Greenland Seas ranged from 0.010 to 1.51%. The high concns. are found in separate areas of brown mud. In all cases the Mn content increases with the fineness of the sediment, and hence with the depth of the sea bed. The accumulation of Mn is favoured by oxidising conditions and high salinity gradients. L. J. J.

Phosphorus in sediments of polar seas. M. V. Klenova and M. L. Budianskaja (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 82—86).—The P distribution in the upper layer of bottom deposits in Polar seas in stations distributed over the Barentz, Kara, and part of the Greenland Seas, was examined. P contents of sediments were in the region 0—0.32% (dry). No correlation with any single condition of sedimentation was found. L. J. J.

Sediments of the Barentz Sea. M. V. Klenova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 796—800).—The sediments are classified according to particle size. The most widespread sediment is sandy mud. The most commonly occurring oxide in it is SiO₂. The concn. of other oxides present varies with the grain size. Analyses are given. A. J. M.

Bacteria in the bottom sediments of the Dead Sea. B. Elazari-Volcani (*Nature*, 1943, 152, 274—275).—Profiles 10 to 170 cm. long were obtained from depths of 70 to 330 m. in the Dead Sea in December, 1941. The layers of colours, indicating zones of sedimentation, showed no seasonal repetition. S₂O₃²⁻-oxidising, cellulose-decomp., very active lactose- and glucose-fermenting, and denitrifying bacteria were found in enriched cultures. E. R. R.

Grude salt deposits in the separation pans of sea basins in the Kara-Bogas-Gol area. V. S. Egorov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 505—508).—The sinking of the level of the Caspian Sea has resulted in a smaller inflow of H₂O into the basins of Kara-Bogas-Gol. This has resulted in a concn. of brine, and in 1939 the first crystallisation of NaCl was observed. Dilution of the brine is necessary for the deposition of sulphates. The increase in concn. of the solution leads to a decrease in separation of mirabilite. The cause of this is discussed. The effect of addition of fresh H₂O to brine on the order in which salts are deposited in the basin is considered. A. J. M.

Unusual occurrence of bedded thenardite. E. Spencer (*Min. Mag.*, 1944, 27, 29—31).—Brine (NaCl 18.5, Na₂SO₄ 6.6, Na₂CO₃ 0.4, NaHCO₃ 0.4%) from shallow wells at Didwana, Jodhpur State, India, is evaporated in salt-pans dug on the surface of the ground, yielding a crop containing NaCl 87.2, Na₂SO₄ 11.2, Na₂CO₃ 0.2, NaHCO₃ 0.1, insol. 0.64, H₂O 0.66%. NaCl:Na₂SO₄ in the brine is 3:1, and in the salt 8:1. In the course of time large deposits of sulphate have accumulated beneath the salt-pans, containing Na₂SO₄ 91.9, NaCl 0.8, insol. 5.7%, etc. Optical data of the well-formed crystals are given. The crit. temp. for the formation of thenardite (anhyd. Na₂SO₄) from a saturated solution of NaCl is 18°, below which the temp. at Didwana rarely falls, when Glauber's salt would be formed. L. J. S.

Presence of leucitic rock in the Kolyma River basin. G. Bilibin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 79—81).—Results of examination of leucitites from the Kolyma River basin in the region of 67° 52' N. lat., 161° 39' E. long., are described. The leucitites alternate with layers of tuff and tuffaceous breccia near a centre of eruptive activity. L. J. J.

Solfataric alteration of rocks at Kilauea volcano. G. A. Macdonald (*Amer. J. Sci.*, 1944, 242, 496—505).—Solfataric alteration of olivine basalt lava and ash at Kilauea Caldera has produced rocks composed mainly of opal with some kaolin, ilmenite, and magnetite. Most of the MgO, CaO, and Na₂O, and much of the Al₂O₃ and Fe₂O₃, have been removed. The vol. and porosity of the rock are practically unchanged, and original structures and textures have been preserved. The alteration resembles that in areas of acid emanations in other volcanic districts. Alteration to limonite and goethite is less abundant. L. S. T.

Attempted revision of the formula of the mineral hibschite. D. S. Beliankin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 420—423).—From analytical data the formula 3(Ca,Mg)O.(Al,Fe)₂O₃.2(Si,Ti)O₂.2H₂O is proposed. W. R. A.

Pickeringite and ferropickeringite—minerals of the pyrite conflagrations in the Urals. G. N. Vertuschkov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 334—336).—Pickeringite (I) and ferropickeringite (II) are minerals produced by underground pyrite conflagrations. They are stable in air, but dissolve readily in H₂O. (I) shows a very thin, parallel, fibrous structure, low double refraction, and has n 1.479. When heated it dissolves in its own H₂O of crystallisation, and fuses to a white, lustrous, brittle bead, which is fairly hard, and has weak magnetic properties. The aq. solution is acidic. (II) forms friable, white, fibrous aggregates, of hardness ≥ 1 , d 1.79. It is readily fusible. After heating in the blowpipe flame, the residue is strongly magnetic. Its empirical formula is (Mg,Fe)Al₂(SO₄)₂.22H₂O. (II) can be distinguished from (I) and from halotrichite only by analysis. The origin of these minerals is discussed. A. J. M.

Occurrence in the Khalilovo iron ore deposits of magnetite formed from solutions of superficial origin at low temperature. B. P. Krotov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 801—803).—The magnetite in these deposits is partly clastic, but pisiform grains, a continuous crust with regular crystals in the cavities at the surface of serpentinites, and veinlets are also found. The pisolitic structures have been formed by pptn. from solutions, part of the Fe₂O₃ having been reduced to FeO by decaying vegetable remains. The magnetite in veinlets originated at the epoch of diagenesis of the sediments of the basin (Jurassic) and their chloritisation. The magnetite in this area is thus of hypogene origin. A. J. M.

Mineralogical aspects of the system FeO-Fe₂O₃-MnO-Mn₂O₃.—See A., 1944, I, 282.

Binary system P_2O_5-2CaO, P_2O_5 .—See A., 1944, I, 281.

Phosphate-siderite rocks of the Turga horizon of Transbaikalia. K. S. Andrianov and A. I. Smirnov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 75—78).—Results of an investigation of the Zaza series in exposures along the Vitim and Zaza Rivers (Lower Cretaceous deposits in the Eravna district of the Buriat-Mongol Republic) are reported. Palaeontological, geological, and mineralogical data for a no. of beds encountered are given. Phosphatised siderites and phosphorites have been formed in a fresh- H_2O lacustrine basin. This is possible in an alkaline reducing medium containing the ions concerned. Reducing conditions are evidenced by abundance of org. matter, pyrites, and bituminous shale. Phosphatised siderites form 24 bands with total thickness 2.5 m. L. J. J.

Ferruginous manganese rocks in the phosphorite-bearing beds of the Kara-tau. P. L. Bezrukov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 433—435).—The Cambrian deposits of Kara-tau show a combination of several chemical sediments: phosphate, siliceous, ferruginous, and Mn. The mode of their accumulation is discussed. W. R. A.

Genesis of the Mazul manganese deposit. G. D. Afanasiev, N. C. Aidinian, and I. V. Borisevitch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 792—795).—The ores occurring in the Mazul deposit are discussed, and the process of ore formation is divided into four stages. The ores are chiefly carbonates, and oxidised Mn and Fe ores. The origin of the deposit appears to be primarily sedimentary, with a subsequent superposition of regional metamorphism. A. J. M.

Axinite from the mine "Julia" of the Khakas province. S. M. Kurbatov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 428—430).—Analysis of axinite confirms Vernadski's formula, viz., $CaB_2Si_2O_8 \cdot 2Ca(Al, Fe)_2Si_2O_8 \cdot 2(Ca, Fe, Mn, Mg, H_2)SiO_4$. W. R. A.

Alkaline rocks of the Kovdor-Ozero region of the Kola peninsula. J. P. Ivensen (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 337—339).—The alkaline rocks in the neighbourhood of Lake Kovdor fall into two groups: (1) alkaline cancrinite and nepheline syenites, and (2) ijolite-urtites. The location of the rocks is given and their origin is discussed. A. J. M.

Relations of clinoenstatite to enstatite and diopside. D. S. Beliankin and B. V. Ivanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 647—648).—Interaction of refractories in an open-hearth furnace gave rise to the formation of large skeleton crystals of clinoenstatite, the surface of which was overgrown with shells of enstatite-diopside (I) in a parallel crystallographic position, and at the edge, passing into yellowish-green augite. This shell-like crystallisation of (I) around clinoenstatite resembles that of microcline around plagioclase. It is suggested that the sequence of crystallisation is governed by temp. A. J. M.

Mineralogy and geochemistry of the lead ore-bearing deposit Mirgalimsai in South Kazakhstan. E. V. Schevtschenko and V. K. Monitsch (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 30—32).—The Mirgalimsai deposit in the Djambul district contains fine-grained disseminated ores bedded in Upper Devonian limestones. The deposit is a tectothermal type connected with the Variscan folding of the Karatau region. A detailed history of the mineralisation process is presented. Elements characteristic of the basal magma (Ni, Co) are absent. Sn, Bi, and As, characteristic of Variscan deposits adjoining Uzbekistan and Kirghizia, are also absent. L. J. J.

Heats of transformation in the systems wurtzite-sphalerite and cinnabar-metacinnabarite.—See A., 1944, I, 282.

Nickel and cobalt in the manganese ores of Chiatura (Georgia). O. E. Zvjagintzev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 180—181).—Recent analyses of the Mn ores of the Chiatura district having an accuracy of 0.0005% of the sample wt. show that both oxide and carbonate ores contain nearly const. amounts of Ni and Co slightly >, and in the ratio of, their Clarke nos. The concn. is independent of the type of ore and the Mn content. J. O'M-B.

Birefringence of gypsum and barytes in the extreme red and near infra-red. J. Jaffray (*Compt. rend.*, 1943, 216, 409—410).—The birefringence $n_y - n_x$ of a sample of gypsum was 0.0092 for Na-D at 17°, and decreased from 0.00917 to 0.00865 over the λ range 6000—8800 Å. at 17°. A barytes sample cut perpendicularly to the acute bisector of optic axes had $n_m - n_p$ 0.00118 for Na-D at 16°, decreasing from 0.001155 to 0.001046 between 6000 and 9000 Å. at 16°. L. J. J.

Isomorphic substitutions in carbonate-apatite. I. Borneman-Starinkevitch and N. Belov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 804—806).—The formula $xCa_{10}P_6O_{24}F_2 + yCa_{10}P_6CO_{23}(F, OH)_2$ corresponds with the % compositions of minerals of the carbonate-apatite class. There is P C substitution. A. J. M.

New mineral species of the platinum group. O. E. Zvjagintzev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 26, 788—791).—Norilsk

Pt differs considerably from Ural Pt in containing a high proportion of Pd (2—14%), Fe (13—26%), Ni (>25.6%), Cu (>9.3%), and some Ag. It is probable that the Pt grains have cryst. out of a gaseous medium which contained carbonyls of Pt, Ni, Fe, Cu, and Pd.

A. J. M.
Serpentine pseudomorphs after actinolite. V. N. Schtscherbina (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 176—177).—An original mineral formation encountered in the Ebeita serpentinite massif is shown to be a large pseudomorph of serpentine after radial actinolite. Its mineralogy is described and its origin is discussed. L. S. T.

Quantitative characteristics of the degree of uniformity of mineralisation, X_{alb} . I. S. Stepanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 511—514).—The degree of uniformity of mineralisation is the ratio of the average metal val. to that of rich ores. The method of calculating this quantity, and some vals. for various deposits, are given. A. J. M.

Adsorption of hardness-reducers by rocks at different concentrations. M. V. Efimov (*J. Appl. Chem. Russ.*, 1940, 13, 1336—1340).—Solutions of NaCl, $MgCl_2$, and $AlCl_3$ become alkaline in contact with powdered granodiorite (felspar + biotite + quartz), the [OH] being in $AlCl_3$ solution > $MgCl_2$ > NaCl. This is correlated with the acceleration of boring observed when NaCl, $MgCl_2$, or $AlCl_3$ is added to H_2O lubricating drills in Au mines. J. J. B.

Content of radioactive elements in some soils of the U.S.S.R. V. I. Baranov and S. G. Zeitlin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, 30, 330—333).—Soils on lat. 40° N. were examined. The content of Ra and Th in all the soils investigated was of the same order, viz., 10—11% Ra and 10—4% Th. The ratio Th/Ra is approx. the same in all cases, the average being 6.9×10^4 , which is approx. the same as the Th/Ra ratio in rocks. The emanation power of the soils was also determined. They all emit an appreciable amount of Rn and Tn. The emanating power is, on the average, 41% Rn and 45% Tn. A. J. M.

Geological conditions of gas accumulations in coal deposits in the Kuznetzk Basin. A. I. Kravsov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 27—29).—The Aralichevo coal deposit of the Stalinsk region is associated with alternating sandstones, aleurolites, argillites, and carbonaceous shales over a thickness of 375 m., containing 12 workable seams 1—8.4 m. thick. The coal contains 7—12% of volatile matter. The deposits are thrown into a large no. of folds and have a high CH_4 content, increasing with depth and in the anticlinal crests, and varying considerably from one fold to another. L. J. J.

Genetic classification of caustobiotites. A. F. Dobrjanski (*J. Appl. Chem. Russ.*, 1940, 13, 443—446).—If the analyses of the org. part of wood and fossil fuels are represented in a triangular diagram with C, H, and (O + S + N) in the summits, it is seen that they form two distinct branches which touch each other at the beginning (at small C contents). To one branch belong wood, peat, lignite, coal, and anthracite; the other includes sapropel, oil shale, sapropelite, asphalt, petroleum, and asphaltites. These facts serve to solve the problem of the origin of petroleum and asphaltites. Petroleum is a derivative of sapropel, and asphaltites are formed by oxidation and evaporation of asphalt and petroleum. J. J. B.

Variation of Ishimbay oils. G. D. Halpern (*Compt. rend. Acad. Sci. U.R.S.S.*, 1943, 41, 167—168).—The deposit is characterised by zonal oil distribution; ρ and η increase regularly from the centre to the periphery. The causes of the variation, and of the variations displayed by a single well at different periods of its life, are discussed. L. S. T.

Prognosis of oil deposits. S. F. Fedorov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 28, 49—54).—Five factors are enumerated as important in forecasting the yield of oil-bearing strata: (i) oil is not found on a commercial scale in horizontally bedded deposits; (ii) the property of acting as an oil reservoir is determined by the "effective porosity" of strata, i.e., the % of pores permitting free movement of oil; (iii) the presence of waters containing $CaCl_2$ and alkali is characteristic of oil-bearing deposits; (iv) the reducing action of oil on rocks produces a fall in the redox potential of deposits as an oilfield is approached; (v) hydrocarbon gases are found in the soil above oil deposits. L. J. J.

Occurrence of oil as related to gravitational anomalies. L. V. Chmelevskaja (*Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 36, 182—184).—A review of the available data. It is concluded that the layers bearing oil in primary deposits are older than the orogenic phase in which the oil originated. Oil is found either on the outskirts of some young orogenic region in a zone of negative anomalies or on the outskirts of ancient orogenic regions in a zone of positive anomalies. In the latter case the oil was first deposited in rocks older than the orogenic phase responsible for the region. Recent movements causing dislocations in the border portion of ancient orogenic regions can change the sign of the anomaly. J. O'M-B.